THE JOURNAL

OF THE

American Chemical Society

VOL. LIII

JANUARY—APRIL
1931

Editor
ARTHUR B. LAMB

Associate Editors

EASTON, PA.
MACK PRINTING COMPANY
1931

The Journal of the
American Chemical Society

VOL. 53 JANUARY, 1931 No. 1

[CONTRIBUTION FROM THE ANIMAL NUTRITION LABORATORY, UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA]

RECALCULATIONS OF THE FIRST DISSOCIATION CONSTANT OF PHOSPHORIC ACID IN AQUEOUS SOLUTION AT 18°, AND INCIDENTAL DETERMINATION OF THE ACTIVITY COEFFICIENTS OF THE UNDISSOCIATED ACID MOLECULES

BY JOSEPH W. H. LUGG

RECEIVED JULY 1, 1930 PUBLISHED JANUARY 12, 1931

In 1907 Noyes and Eastman[1] measured the formula conductivities of phosphoric acid in aqueous solutions of low concentration at 18°, and in 1909 Abbott and Bray[2] used these data in conjunction with their own determination of the equivalent conductivity at infinite dilution of $H^+ + H_2PO_4^-$ ions, in calculations of the first stoichiometric dissociation constant. It appears that no reliable conductivity measurements of dilute phosphoric acid solutions have been made since then.

Sherrill and Noyes[3] in 1926 recalculated the first constant from Noyes and Eastman's data and by way of correcting for inter-ionic electrical effects they made use of the fact noted by MacInnes,[4] namely, that mobilities of certain monatomic univalent ions (K^C, Na^C, Cl^-, etc.), up to about 0.1 N concentration, are independent of the oppositely charged ions associated with them provided these latter are monatomic and univalent.

In their recalculations of the original data, Sendroy and Hastings[5] did not correct for inter-ionic attraction forces. They calculated the ionic strengths of the solutions from the original phosphoric acid molarities instead of from the equivalent ion concentrations.

Onsager's[6] admirable development of the Debye–Hückel theory[7] furnishes means for correcting the measured conductivities of the phosphoric acid solutions for inter-ionic attraction forces. For completely dissociated

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[1] Noyes and Eastman, Carnegie Inst. Washington Publ. No. 63, 1907, p. 262.

[2] Abbott and Bray, THIS JOURNAL, 31, 729 (1909).

[3] Sherrill and Noyes, *ibid.*, 48, 1861 (1926).

MacInnes, *ibid.*, 43,1217 (1921).

[5] Sendroy and Hastings, J. *Biol.* Chem., 71, 783 (1927).

[6] Onsager, *Physik*. Z., 28, 277 (1927).

[7] Debye and Hückel, *Physik. Z.*, 24, 305 (1923).

uni-univalent electrolytes in aqueous solution at 18°, Onsager's limiting equation is

$$A = A, - (35.7 + 0.159\Lambda_\infty)\sqrt{2c} \qquad (1)$$

where A is the equivalent conductivity at concentration c and **A,** is the equivalent conductivity at infinite dilution. Practically all modern evidence weighs in favor of the contention that strong electrolytes such as NaCl, KCl, LiCl, HCI, KOH, etc., and many of higher valence type, are completely dissociated in aqueous solution, even up to molar concentration. To conductivity data for the uni-univalent electrolytes, Debye and Hiickel[8] have applied equations of the form

$$A = \Lambda_\infty - a\sqrt{2c} + b2c \qquad (2)$$

determining the constants *a* and b for each electrolyte by the method of least squares. It may be concluded from Onsager's paper that a negative value for b connotes incomplete dissociation.

The *a* values agree excellently with the Onsager theoretical coefficients, so the assumption that an equation of the form of (2) would apply to solutions containing only H^+ and $H_2PO_4^-$ ions necessarily in equal concentration is well founded. With the value of A, at 18° known, *a* could be calculated from Equation 1, and b may be assigned the rough value +40, from a consideration of the positive Debye–Hiickel coefficients.

Determination of A, ($H^+ + H_2PO_4^-$) at 18°

The quantity μ which occurs frequently in this paper is not quite the same as the "ionic strength" as defined by Lewis and Randall,[9] but is defined in the identity, $\mu \equiv {}^1/_2\Sigma(Cz^2)$, where C is the concentration of an ion in moles per liter, and z is its valence. "μ" defined in this way has greater significance in the Onsager and Debye–Hiickel equations.

In arriving at a value for Λ_∞ ($H^+ + H_2PO_4^-$), the conductivity data of Abbott and Bray[2] for the salt NaH_2PO_4 were employed, but were first corrected for dissociation of the $H_2PO_4^-$ ions. The corrections were considerably smaller than those calculated by Abbott and Bray. A generalized equation for the second stoichiometric dissociation constant of phosphoric acid and rough values for the mobilities of the ions H^+, $H_2PO_4^-$ and $HPO_4^=$, used in calculating the corrections to be applied to A NaH_2PO_4 as measured, appear below

$$pK_2 = 7.16 - \frac{2\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} \qquad (3)$$

$\Lambda_\infty H^+ = 314$; $\Lambda_\infty H_2PO_4^- = 27$; $\Lambda_\infty {}^1/_2HPO_4^= = 53$. Decreases in these values with increase in μ are calculable from the Onsager equations.

Equation **3** has been deduced by the author from his own data for the

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[8] Debye and Hückel, *Physik. Z.*, 24, *305 (1923).*

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

second constant[10] and from the data in W. Mansfield Clark's 1928 edition of "The Determination of Hydrogen Ions." From these sources it is found that in presence of most salts, $p\overline{K}_2$ (*i. e.*, $pK_2 + p\gamma_{\mathrm{H}^+}$) $= 7.16 - 1.5\sqrt{\mu}/1 + a\sqrt{\mu})$ at 18°, where p signifies negative common logarithm, γ_{H^+} is the activity coefficient of H^+ ion, and a is a constant determined by the ionic environment. Replacing $p\gamma_{\mathrm{H}^+}$ from Equation 12 of this paper, one obtains for pK_2 at 18°, the approximate equation $pK_2 = 7.16 - 2\sqrt{\mu}/(1 + a\sqrt{\mu})$. The most likely value for a in NaH_2PO_4 solutions seems to be about 1.5, but the uncertainty will not materially affect the calculations.

Where d is the degree of dissociation of the $H_2PO_4^-$ ion, calculated with the help of Equation **3,** we have

$$\Lambda_{\text{corr.}}\ \mathrm{NaH_2PO_4} = \Lambda\mathrm{NaH_2PO_4} - d\Lambda\mathrm{H^+} - 2d\Lambda{}^1/{}_2\mathrm{HPO_4^=} + d\Lambda\mathrm{H_2PO_4^-}$$

Table I contains the data of Abbott and Bray for NaH_2PO_4 conductivity; corrections to be applied for secondary dissociation of the H_2PO_4 ions; corrected values of ΛNaH_2PO_4; values of μ; and values of $\sqrt{\mu}$.

TABLE I

EQUIVALENT CONDUCTIVITY OF NaH_2PO_4 AT 18°

Molarity of NaH_2PO_4	Approx. $\sqrt{\mu}$	Molar conductivity (measured), ΛNaH_2PO_4	Corrn.	Corr. molar or equivalent conductivity, $\Lambda_{\text{corr.}}$ NaH_2PO_4
0	0			70.1[a]
0.001	0.032	71.68 ?	−3.8	67.9
.003	.055	69.23	−2.4	66.8
.005	.071	67.58	−1.8	65.8
.010	.100	65.53	−1.1	64.4
.020	.141	61.43 ?	−0.7	61.7
.050	.229	58.26	− .5	57.8
.100	.316	54.43	− .3	54.1
.200	.447	49.74	− .2	49.5

[a] **Extrapolated.**

Corrected values of Λ were plotted against corresponding values of $\sqrt{\mu}$, and the curve drawn was extrapolated from the points for lowest concentrations almost linearly with $\sqrt{\mu}$ to the point, $\sqrt{\mu} = 0$, $\Lambda_{\text{corr.}} = 70.1$. Slopes of tangents to the curve at low $\sqrt{\mu}$ values corresponded very well with the slope of the theoretical limiting straight line, $\Lambda = 70.1 - (35.7 + 0.159 \times 70.1)\sqrt{2\mu}$, divergences being in the direction expected for a completely dissociated salt.

For Λ_∞NaCl, the value 108.9 determined by Debye and Hückel[8] from the data of Kohlrausch and Maltby was accepted. A value 379.3 for Λ_∞HCl was obtained from the data of Goodwin and Haskell[11] by extra-

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[10] Not **yet published.**

[11] Goodwin and **Haskell,** *Phys.* ***Rev.*,19,369** (1904).

polating to $\sqrt{\mu} = 0$ a curve connecting A with $\sqrt{\mu}$, just as in the case of NaH_2PO_4.

These values of Λ_∞ for the three electrolytes, NaH_2PO_4, NaCl and HCl, are for 18°, and A, $(H^+ + H_2PO_4^-)$ at 18° is readily obtained from 379.3 + 70.1 − 108.9, giving 340.5.

Thus the equation one would expect to apply to aqueous solutions at 18° containing only H^+ and $H_2PO_4^-$ ions is

$$A = A, \; -(35.7 + 0.159 \times 340.5)\sqrt{2e} + 40 \times 2e, \text{ that is}$$

$$A = A, \; - 127.1 \sqrt{e} + 80e \qquad (4)$$

where e is the equivalent ion concentration and A refers to a dilution $1/e$.

Although the second term ($80e$) is not negligible, it is obviously small compared with the first ($127.1 \sqrt{e}$) up to e = 0.04, so the uncertainty attached to the coefficient 80 will be found scarcely to affect the calculations below that value of e.

Calculation of the First Stoichiometric Dissociation Constant.—In aqueous solution phosphoric acid dissociates as follows

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-; \quad H_2PO_4^- \rightleftharpoons H^+ + HPO_4^=; \quad HPO_4^= \rightleftharpoons H^+ + PO_4^{\equiv}$$

For any but almost infinitely dilute solutions of the free acid, the magnitudes of the three dissociation constants are such as to allow the production of only H^+ and $H_2PO_4^-$ ions in any appreciable quantity. OH^- ion concentrations, of course, are negligibly small in consequence of the hydrogen ionization of the acid. Thus the conductivity of phosphoric acid solutions down to a molarity of, say, 0.0001 may be considered due entirely to the presence of H^+ and $H_2PO_4^-$ ions in equal concentration. Hence where A is the molar conductivity at molarity c of a solution of phosphoric acid at 18°, and d is the degree of the first dissociation, we have, neglecting viscosity changes which are small enough at low concentrations

$$\Lambda/d = A, \; (H^+ + H_2PO_4^-) - A\sqrt{dc} + Bdc \qquad (5)$$

where A is 127.1 and B is 80. Transposition, squaring of both sides and subsequent rearrangement lead to

$$(B^2c^2)d^4 + (2B\Lambda_\infty - A^2c)d^3 - (2B\Lambda c - \Lambda_\infty^2)d^2 - (2\Lambda\Lambda_\infty)d + \Lambda^2 = 0 \qquad (6)$$

Certain roots of this biquadratic in d would have to be excluded and it must be recalled that only the positive extraction of $\sqrt{dc}$ in Equation 5 is to be used.

Defining $A_{,,,,}$ in the relation $\Lambda_{corr.}/\Lambda_\infty = d$, and substituting in Equation 5, one obtains

$$A_{,,,,.} = A + Ad\sqrt{dc} - Bd^2c \qquad (7)$$

and $A_{,,,,}$ is A corrected for inter-ionic attraction forces. From Equation 7 $A_{,,,}$ may be obtained by a series of successive approximations and then d may be calculated from the definition. Two such approximations were found sufficient to give values of $\Lambda_{corr.}$ unaltered in the first decimal place by successive approximations, and values of d appearing in

Table II were derived from these instead of from laborious solution of Equation 6.

By the law of mass action we have for the first stoichiometric dissociation constant, square brackets signifying molarities

$$K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{dcdc}{(1-d)c} = \frac{d^2c}{(1-d)} \tag{8}$$

In logarithmic form, where p signifies negative common logarithm, Equation 8 becomes

$$pK_1 = p[H^+] + p[H_2PO_4] - p[H_3PO_4] = 2pd + pc - p(1 - d) \tag{9}$$

Table II contains in the order of the columns, the data of Noyes and Eastman, corrections to A, $\Lambda_{corr.}$, d, μ, $\sqrt{\mu}$, K_1 and pK_1.

TABLE II

Original H_3PO_4 molarity, c	A	Corrn.	$\Lambda_{corr.}$	$d = \frac{\Lambda_{corr.}}{\Lambda_\infty}$	$\mu = e = dc$	$\sqrt{\mu}$	$K_1 = \frac{d^2c}{(1-d)}$	pK_1
0				1.0000	0	0	0	2.090[a]
0.0002	330.8	1.8	332.6	0.9769	0.0001954	0.0140	0.00826	2.083
.0020	283.1	4.3	287.4	.8441	.001688	.0411	.00915	2.039
.0100	203	5.9	208.9	.6136	.006136	.0783	.00974	2.011
.0125	191.2	6.0	197.2	.5791	.007239	.0851	.00997	2.001
.0500	122.7	6.0	128.7	.3780	.01890	.1375	.01149	1.940
.0800	104	6.0	110.0	.3231	.02585	.1608	.01234	1.909
.1000	96.5	5.9	102.4	.3008	.03008	.1734	.01294	1.888

[a] Extr.

The Constant at Infinite Dilution. Activity Coefficients of H_3PO_4.—By definition and the mass law, the first activity dissociation constant of phosphoric acid K'_1 is given in Equation 10 and is an exact constant. α_X signifies activity of X, and $\alpha_X = \gamma_X[X]$, where γ_X is the activity coefficient, expresses its relation to the molarity. The chosen standard state in which $\gamma_X = 1$ (*i. e.*, $\alpha_X = [X]$) for H^+, $H_2PO_4^-$, and H_3PO_4, is infinite dilution in each case.

$$K'_1 = \frac{\alpha_{H^+} \times \alpha_{H_2PO_4^-}}{\alpha_{H_3PO_4}} \tag{10}$$

Hence replacing α_X by $\gamma_X[X]$ and expressing in logarithmic form

$$pK'_1 = p[H^+] + p[H_2PO_4] - p[H_3PO_4] + p\gamma_{H^+} + p\gamma_{H_2PO_5} - p\gamma_{H_3PO_4}$$

Substitution from Equation **9** followed by rearrangement, gives

$$pK_1 = pK'_1 - p\gamma_{H^+} - p\gamma_{H_2PO_4^-} + p\gamma_{H_3PO_4} \tag{11}$$

For variation of the activity coefficient of an ion with μ, the Debye-Hückel[12] equation has been found to apply admirably up to $\mu = 0.5$ or more

$$p\gamma_i = \frac{0.5\, z_i^2 \sqrt{\mu}}{1 + 3.3 \times 10^7 a_i \sqrt{\mu}} \tag{12}$$

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[12] Debye-Hückel, *Physik. Z.*, *24*, 185 (1923).

where z_i is the valence of the ion and a_i is the mean limit of approach of ions to ions of kind "i."[13] In place of 3.3 X $10^7 a_i$ one may use the coefficients a for H^+ and b for $H_2PO_4^-$ ions, in solutions containing H^+ and $H_2PO_4^-$ ions. Then $-p\gamma_{H^+} - p\gamma_{H_2PO_4^-}$ may be put in the form

$$\frac{-0.5\sqrt{\mu}}{1 + a\sqrt{\mu}} + \frac{-0.5\sqrt{\mu}}{1 + b\sqrt{\mu}}$$

and provided a and b be of the same order of magnitude the expression may be reduced for practical purposes to

$$-\frac{\sqrt{\mu}}{1 + a\sqrt{\mu}}$$

where a now has some mean value. The expression approaches $-\sqrt{\mu}$ as $\sqrt{\mu} \longrightarrow 0$.

Debye and McAulay[14] have investigated variation of the activity coefficient of a non-electrolyte in presence of an electrolyte, and have deduced a theoretical equation which may be expressed

$$p\gamma_{\text{non-elect.}} = -S\mu \qquad (13)$$

where S is a constant depending upon the mean effective ionic radius, among other things. Experimentally, it has been shown by these authors and by Randall and Failey[15] that the variation depends almost entirely upon the concentration of electrolyte and scarcely at all upon the concentration of non-electrolyte up to moderate concentrations, and is, moreover, in agreement with the general equation. One may therefore replace $p\gamma_{H_3PO_4}$ in Equation 11 by $-S\mu$, where S is a constant. Equation 11 becomes

$$pK_1 = pK_1' - \frac{\sqrt{\mu}}{1 + a\sqrt{\mu}} - S\mu \qquad (14)$$

$dpK_1/d\sqrt{\mu} = -1/(1 + a\sqrt{\mu})^2 - 2S\sqrt{\mu}$, giving slopes of tangents to the curve of Equation 14 and showing that the slope is -1 when $\sqrt{\mu} = 0$.

Values of pK_1 appearing in Table II were plotted against corresponding values of $\sqrt{\mu}$, but practically no weight was placed upon the point corresponding with lowest phosphoric acid concentration, because A, and A„„ cannot be known exactly and for this point it requires an error of but ±0.1 in either to effect an error of ± 0.01 in pK_1. **A** smooth curve was drawn with tangential slopes continually approaching -1 as $\sqrt{\mu}$ decreased to zero.[16] pK_1 at $\sqrt{\mu} = 0$ (*i. e.*, pK_1') was found to be 2.09. The values obtained by Sherrill and Noyes and by Sendroy and Hastings, are 2.08 and 2.11, respectively.

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[13] The additional "salting out term," $(-C\mu)$, deduced by Hückel [*Physik.* Z., 26,931 (1925)], where Cis small and positive, may well be omitted here since its effects would be inappreciable up to $\sqrt{\mu} = 0.2$. A very small increase in the value of a_i compensates for the omission up to much higher values of $\sqrt{\mu}$.

[14] Debye and McAulay, *ibid.*, 26, 22 (1925).

[15] Randall and Failey, *Chem.* Reviews, 4, 271 (1927).

[16] When S is positive, Equation 14 permits such a smooth extrapolation only provided that $S > a$. The condition is satisfied in this case.

In Fig. 1 are shown the curve connecting pK_1 with $\sqrt{\mu}$ and passing through the point $pK_1 = 2.09$, $\sqrt{\mu} = 0$, the limiting straight line $pK_1 = 2.09 - \sqrt{\mu}$, and a curve $pK_1 = 2.09 - \sqrt{\mu}/(1 + 1.0\sqrt{\mu})$. The choice of a value 1.0 for a in Equation 14 is suggested from an examination of scattered data for different electrolytes, and it is considered unlikely to be in error by more than +0.5 or −0.3. From the divergence of the two curves in the figure, S in Equation 14 is readily calculated to be 1.8 An error of ±0.3 in the chosen value for a, would result in an error of about ±0.2 in the calculated value of *S*. With the assumed value 1.0 for a, therefore, the equation connecting pK_1 for pure phosphoric acid in dilute aqueous solution at 18°, with μ calculated from the H^+ and $H_2PO_4^-$ ions, is

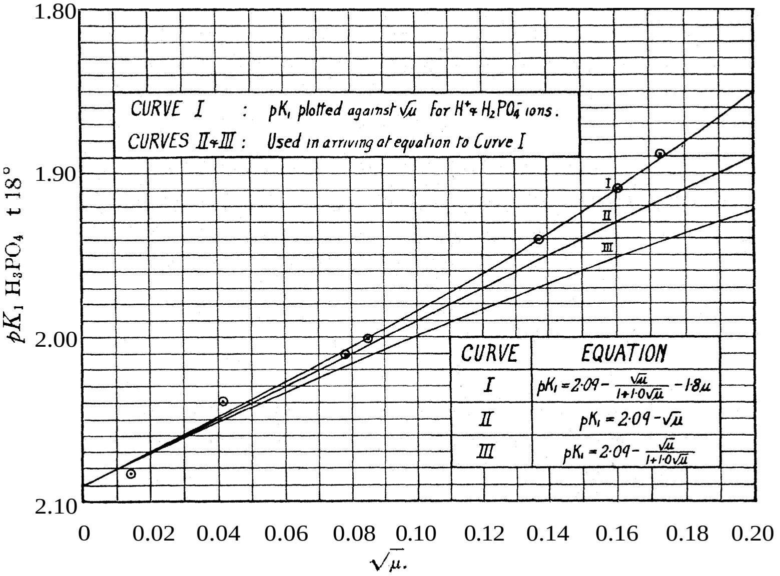

Fig. 1.

$$pK_1 = 2.09 - \frac{}{1 + 1.0\sqrt{\mu}} - 1.8\mu \tag{15}$$

making the equation for the activity coefficient of undissociated phosphoric acid in presence of H^+ and $H_2PO_4^-$ ions in aqueous solution at 18°.

$$p\gamma_{H_3PO_4} = -1.8\mu \tag{16}$$

In conclusion the author wishes to acknowledge his indebtedness to Dr. S. W. Pennycuick of the Adelaide University for reading the manuscript and suggesting alterations, and making the necessary arrangements for publication.

Summary

1. From data in the literature it has been found that Λ_∞ NaH_2PO_4 is 70.1 at 18°, and from this and the values 108.9 and 379.3 for A, NaCl and

Λ_∞HCl, respectively, Λ_∞ ($H^+ + H_2PO_4^-$) has been calculated to be 340.5 at that same temperature.

2. Values for the first stoichiometric dissociation constant of phosphoric acid alone in aqueous solution at 18° have been calculated from the data of Noyes and Eastman. pK_1' (*i. e.*, pK_1 at infinite dilution) has been assigned the value 2.09. An equation well fitting the data is $pK_1 = 2.09 - \sqrt{\mu}/(1 + 1.0\sqrt{\mu}) - 1.8\mu$.

3. An approximate equation for the activity coefficient of the undissociated fraction in pure dilute aqueous solutions of phosphoric acid at 18° is $p\gamma_{H_3PO_4} = -1.8\mu$, where μ is calculated from the equivalent ion concentration.

[Contribution from the Department of Chemistry, Yale University]

THE TEMPERATURE COEFFICIENT OF DISSOCIATION OF ACETIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS[1]

By Herbert S. Harned and George M. Murphy

Received July 15, 1930 Published January 12, 1931

It has been shown by Harned and Robinson, and Harned and Owen[2] that the ionization constant, hydrogen- or hydroxide-ion concentrations, and ionic activity coefficients of weak acids and bases may be determined from measurements of cells without liquid junction. Their measurements were all made at 25°. Since it is a matter of considerable importance to study the effect of temperature on the dissociation of a weak electrolyte both in a pure solvent and in salt solutions, the present study was undertaken. To this end accurate measurements of the cells

$$H_2 \mid HCl\ (0.01),\ MCl\ (m) \mid AgCl \mid Ag, \text{ and} \qquad (I)$$
$$H_2 \mid HAc\ (0.2),\ MCl\ (m) \mid AgCl \mid Ag \qquad (II)$$

at 20, 25 and 30° have been made, in which HAc is acetic acid, and MCl sodium and potassium chlorides.

Experimental Procedure and Results

The cells employed were of the usual H-type, and were equipped with a three-way stopcock through which the hydrogen entered the cell. By the proper manipulation of this stopcock, the cell could easily be transferred from a thermostat maintained at one temperature to one at another temperature without danger of the hydrogen electrode coming into contact with air. Equilibrium in the cell was considered established when

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[1] The present investigation represents part of the thesis presented by George M. Murphy in partial fulfilment of the requirements for the degree of Doctor of Philosophy, Yale University, 1930.

[2] Harned and Robinson, This Journal, 50, 3157 (1928); Harned and Owen, *ibid.*, 52, 5079 (1930).

the readings of the electromotive force were constant to ±0.02 mv. Cells of this type without employing a vacuum technique are reproducible to within ±0.2 mv. The mean temperature coefficients may be reproduced to within ±0.005 mv.

TABLE I

(1) ELECTROMOTIVE FORCES OF CELLS

H_2 | HCl (0.01), MCl (m) | AgCl | Ag

MCl = KCl

M	E_{20}	E_{25}	E_{30}	10^6a_{25}	10^6b_{25}
0.00	0 46359	0.46456	0.46533	374.55	−86.1
.05	.42359	.42394	.42400	96.71	−13.7
.1	.41060	.41068	.41058	− 4.87	− 8.8
.2	.39585	.39575	,39537	−121.29	−14.15
.5	.37628	.37588	.37526	−271.36	−11.71
1	.35820	.35754	.35664	−436.31	−13.43
1.5	.34668	.34582	.34475	−558.09	−12.15
2	.33691	.33591	.33471	−654.94	−11.91
3	.32175	.32055	.31914	−814.2'3	−13.11)

MCl = NaCl

M	E_{20}	E_{25}	E_{30}	10^6a_{25}	10^6b_{25}
0.05	0.42327	0.42361	0.42375	113.31	− 9.44
.1	,41021	.41030	.41025	9.75	− 6.82
.2	.39568	,39552	.39524	−111.25	− 6.07
.5	.37503	.37458	.37404	−264.30	− 4.81
1	.35541	.35473	.35393	−417.22	− 6.77
1.5	.34170	.34088	.33991	−525.11	− 8.80
2	.32973	.32879	.32772	−611.33	− 7.91
3	.30984	,30866	.30738	−796.99	− 6.48

(2) ELECTROMOTIVE FORCES OF THE CELLS

H_2 | HAc (0.2), MCl (*m*) | AgCl | Ag

HAc = CH_3COOH, MCl = KCl

M	E_{20}	E_{25}	E_{30}	10^6a_{25}	10^6b_{25}
0.05	0.46451	0.46540	0.46618	356.68	−5.16
.1	.44901	.44962	.45012	241.00	−4.45
.2	.43298	.43294	.43325	154.76	−2.31
.5	.41174	.41170	.41158	− 38.86	−3.89
1	.39444	.39406	.39356	−223.32	−6.09
1.5	.38451	.38394	.38324	−333.39	−7.29
2	.37702	,37632	.37550	−406.57	−7.44
3	.36576	.36492	.36396	−493.26	−6.58

MCl = NaCl

M	E_{20}	E_{25}	E_{30}	10^6a_{25}	10^6b_{25}
0.05	0.46378	0.46475	0.46564	398.06	−3.87
.1	.44792	.44860	.44920	285.33	−3.57
.2	.43146	.43188	.43220	171.34	−4.63
.5	.40938	.40940	.40935	− 73.28	−3.42
1	.39050	.39024	.38984	−171.69	−5.64
1.5	37862	.37815	,37756	−280.31	−5.29
2	.36868	.36804	.36732	−366.81	−4.89
3	.35308	,35222	.35126	−513.88	−6.25

In Table I are given the observed electromotive forces of the cells designated at 20, 25, and 30°.

The frequently employed equation

$$E_t = E_{25}\,(1 + a_{25}\,(t - 25) + b_{25}\,(t - 25)^2) \qquad (1)$$

is sufficient to express the electromotive force as a function of t. The constants a_{25} and b_{25} are given in the fifth and sixth columns of the table.

The Activity Coefficients and Partial Heat Content **of** Hydrochloric Acid in the Chloride Solutions.—The activity coefficient of the acid in the salt solutions may be computed from the well-known equation

$$\ln \gamma = \frac{E_0 - E}{2RT} F \ln \gamma_0 - \ln \frac{\sqrt{0.01(0.01 + m)}}{0.01} \qquad (2)$$

where E is the electromotive force of the cell containing salt, E_0 that of the cell containing acid only, and γ_0, the activity coefficient of the acid of 0.01 M concentration at a temperature T.

According to the computations of Randall and Young,[3] the activity coefficient of ±0.01 M acid at the freezing point of the solution differs by 0.2% from that at 25°. Fortunately, sufficient heat data are available to estimate the variation of γ_0 with the temperature in the neighborhood of 25°. The variation of the activity with the temperature is given by

$$\frac{\mathrm{d} \ln a}{\mathrm{d}T} = -\frac{\bar{L}}{RT^2} \qquad (3)$$

where $\bar{L}$ is the partial heat content relative to o at zero concentration of solute. The variation of $\bar{L}$ with temperature may be represented by the equation

$$\bar{L} = \bar{L}_{25} + (\bar{C}_p - \bar{C}_p^{\circ})\,(T - 298.1) \qquad (4)$$

where $\bar{C}_p$ and $\bar{C}_p^{\circ}$ are the partial molal heat capacities of the solute at concentrations m and o, respectively, and $\bar{L}_{25}$ is the relative partial heat content at 25°. Substituting this expression in Equation 3 and performing the integration, it is found that

$$\log \frac{a_{25}}{a_t} = -\bar{L}_{25}y + \Delta C_p z \qquad (5)$$

where

$$y = \frac{298.1 - T}{2.303 \times 298.1 \times RT} \qquad (6)$$

and

$$z = 298.1y - \frac{1}{R} \log \frac{298.1}{T} \qquad (7)$$

Values of y and z have been computed and tabulated by Lewis and Randall.[4] Since

$$\log a = 2 \log a, = 2 \log my \qquad (8)$$

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

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 613–616.

we readily find that

$$\log \frac{\gamma_{25}}{\gamma} = -\frac{1}{2}(\bar{L}_{25}y - \Delta C_p Z) \qquad (9)$$

The value of $\bar{L}_{25}$ for 0.01 M hydrochloric acid has been computed by Harned[5] from the electromotive force measurements of Ellis, and Noyes and Ellis[6] and is 78.9 calories. The values of C_p and C_p° have been determined calorimetically by Randall and Ramage[7] and are: $\bar{C}_p^\circ = -41$; $\bar{C}_p = -41 + 14m^{1/2} = -39.6$, whence $\Delta\bar{C}_p = 1.4$ cal. Substituting these values in (9) and performing the calculation, we find that the value of the ratios, γ_{25}/γ_{20} and γ_{30}/γ_{25} is 0.999, corresponding to a variation of about 0.1% for a change in temperature of 5°. Since only a 0.2% variation is obtained in going from the freezing point of the acid at 25° and 0.1% for 5° change, it appears that γ is changing most rapidly in the neighborhood of 25° provided that the method of extrapolation from the freezing point data is accurate. Since the change in γ_0 with the temperature at the concentration in question is so small, and because of the uncertainty in the heat data, we have taken γ_0 to be the same at 20, 25 and 30°. The value used was 0.902,[8] which upon substitution in Equation 2 gives

$$\log \gamma = \frac{2520}{T}(E^\circ - E) - 0.04479 - \log \frac{\sqrt{0.01(0.01 + m)}}{0.01} \qquad (10)$$

The activity coefficients given in Table II were computed by this equation from the electromotive forces in the first half of Table I.

The data in the table show that γ decreases slightly with the increase of temperature and that this decrease becomes greater at higher salt concentrations. Such a decrease of y is to be expected.

If we substitute the value for the free energy of the cell reaction derivable from Equation 1 in the Gibbs–Helmholtz equation

$$\frac{d(-\Delta E/T)}{dT} = \frac{\Delta H}{T^2} \qquad (11)$$

we obtain

$$-\Delta H_{25} = \Delta F_{25}(1 - 298a_{25}) \qquad (12)$$ [9]

by means of which the heat content of the cell reaction at all salt concentrations may be computed. By subtracting the values of $(-\Delta H)_{25}$ at a given salt concentration, M, from the value at zero salt concentration, we obtain the heat content change corresponding to the transfer

$$\text{HCl } (0.01), [\text{MCl}(m)] = \text{HCl } (0.01)$$

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[5] Harned, in Taylor, "Treatise on Physical Chemistry," D. Van Nostrand and Co., New York, 1924, Chap. XII, p. 723.

[6] Ellis, THIS JOURNAL, 38,737 (1916); Noyes and Ellis, *ibid.*, 39,2352 (1917).

[7] Randall and Ramage, *ibid.*, 49, 93 (1927).

[8] Harned and Åkerlöf, *Physik. Z.*, 27,411 (1926).

[9] Ellis, THIS JOURNAL, 38,737 (1916).

TABLE II

ACTIVITY COEFFICIENTS AND RELATIVE PARTIAL HEAT CONTENT OF 0.01 M HYDROCHLORIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

m	γ_{20}	γ_{25}	γ_{30}	$(-\Delta\overline{H})_{25}$, cal.
		MCl = KCl		
0.0	0.902	0.902	0.902	0
.05	.813	.812	.812	46
.1	.777	.776	.776	65
.2	.753	.751	.751	122
.5	.711	.710	.708	291
1	.723	.720	.719	400
1.5	.743	.740	.738	433
2	.781	.778	.775	518
3	.862	.857	.853	663
		MCl = NaCl		
0.05	0.818	0.817	0.816	155
.1	.783	.782	.780	111
.2	.756	.755	.752	188
.5	.730	.728	.724	398
1	.765	.761	.756	640
1.5	.822	.815	.810	853
2	.901	.894	.886	1108
3	1.091	1.081	1.069	1418

or the partial heat content of the acid in the salt solution relative to its value at zero salt concentration.[10] The values of $(-\Delta\overline{H}_{25})$ are given in the fifth column of Table II, and are plotted in Fig. 1 along with values

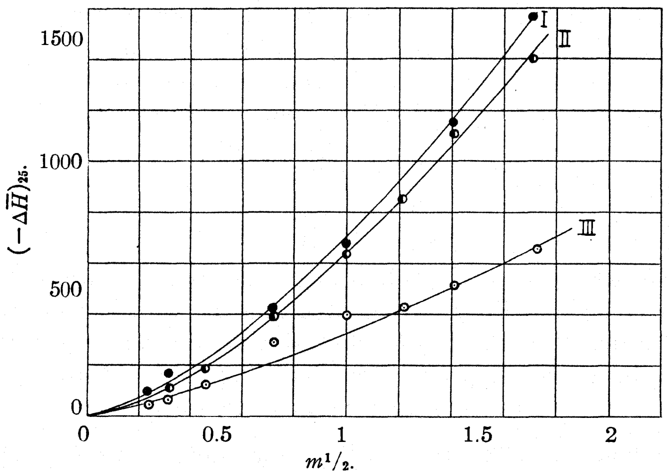

Fig. 1.—The relative partial heat content of hydrochloric acid in potassium and sodium chloride solutions. ●, HCl; ◐, HCl in NaCl; ⊙, HCl in KCl.

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[10] Harned, THIS JOURNAL, 42, 1808 (1920).

for the partial heat content of the pure aqueous acid solution relative to 0.01 M. These latter were taken from the results computed by Harned from the data of Ellis, and of Noyes and Ellis.[5,11] The results appear reasonable and agree in magnitude at least with the less accurate results obtained by Harned.[10] In fact, great accuracy is not to be expected since an error of 0.01 mv. in the temperature coefficient of the cell causes an error of 130 calories in the partial heat content.

The Dissociation of Acetic Acid in Sodium and Potassium Chloride Solutions and its Temperature Coefficient.—From the electromotive forces of cells given in Table I, we may readily obtain those of the cells

$$\text{Ag} \mid \text{AgCl} \mid \text{HCl}\ (0.01) \mid \text{H}_2 \mid \text{HAc}\ (0.2),\ \text{MCl}\ (m) \mid \text{AgCl} \mid \text{Ag}$$

The electromotive forces of the latter are given by

$$E = E_1 - E_0 = 0.00019844\ T \log \frac{(0.902)^2\ (0.01)^2}{\gamma_{\text{H}}\gamma_{\text{Cl}} m_{\text{H}} m} \tag{13}$$

It is important to note that $\gamma_{\text{H}}\ \gamma_{\text{Cl}}$ is the activity coefficient of hydrochloric acid in a solution containing both the weak acid and the salt. Harned and Owen[2] have carefully analyzed Equation **13.** If the values of $\gamma_{\text{H}}^{\circ}\ \gamma_{\text{Cl}}^{\circ}$ obtainable from Table II are substituted in (13), an "apparent" hydrogen-ion concentration, m'_{H}, is obtained because these values of $\gamma_{\text{H}}^{\circ}\ \gamma_{\text{Cl}}^{\circ}$ are obtained in pure aqueous salt solutions and do not equal similar values obtained in the presence of undissociated acetic acid. By introducing $\gamma_{\text{H}}^{\circ}\ \gamma_{\text{Cl}}^{\circ}$ for $\gamma_{\text{H}}\ \gamma_{\text{Cl}}$ in Equation **13,** we obtain

$$\log m'_{\text{H}} = -\frac{E}{0.00019844T} - 4.09858 - 2 \log \gamma_{\text{HCl}}^{\circ} - \log m \tag{14}$$

Further, from Equation 17 of Harned and Owen's study, we find that the relation between the real and apparent hydrogen-ion concentration at a given-temperature is

$$SM = \log \frac{m'_{\text{H}}}{m_{\text{H}}} \tag{15}$$

where S is a constant which corrects for the effect of the undissociated acetic acid molecule, and M is the concentration of the acetic acid. They found that S equals 0.047 and, consequently, SM equals 0.0094. By combining (14) and (15), we obtain

$$\log m_{\text{H}} = -\frac{E}{0.00019844T} - 4.09858 - 2 \log \gamma_{\text{HCl}}^{\circ} - \log m - 0.0094 \tag{16}$$

by which the values of m_{H} contained in Table III were computed in the manner described by Harned and Robinson. In making this step, we have assumed that SM is the same at 20, 25 and 30°. This assumption involves no error greater than the experimental, since M is not high and since the temperature range under consideration is only ten degrees.

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[11] See Chap. XII, Table VII, p. 723, of Taylor's "Treatise on Physical Chemistry." D. Van Nostrand and Co., New York, 1924.

TABLE III

HYDROGEN-ION CONCENTRATIONS OF 0.2 M ACETIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

MCl = KCl				MCl = NaCl			
m	m_{H20}	m_{H25}	m_{30}	m	m_{H20}	m_{H25}	m_{30}
0.05	0.002323	0.002337	0.002339	0.05	0.002361	0 002367	0.002363
.1	.002352	.002364	,002366	.1	.002418	,002424	.002424
.2	,002399	.002415	.002410	.2	,002492	,002495	,002497
.5	,002451	,002476	.002486	.5	.002562	,002574	.002583
1	,002354	.002385	.002405	1	.002462	,002482	.002501
1.5	.002203	.002234	.002259	1.5	.002281	,002309	,002330
2	.002009	.002039	,002065	2	.002104	,002134	.002160
3	.001718	.001746	.001765	3	.001772	.001802	,001830

Our next step is to obtain values for the dissociation constant of the acetic acid at 20, 25 and 30°. Conductance data at temperatures other than 25° are unreliable although they indicate little change of the dissociation constant with temperature in the neighborhood of 25°. We have very good evidence to show that this is the case. The dissociation constant, K, is given thermodynamically by

$$K = \frac{\gamma_{HAc}}{\gamma_H \gamma_{Ac}} \frac{m_H^2}{0.2 - m_H} = \gamma_A^2 K_c \qquad (17)$$

Taking the logarithm, we obtain

$$\log K = \log Kc + 2\log \gamma_A \qquad (18)$$

But we know that in dilute and moderately concentrated solutions the variation of γ_A with the ionic strength is given by

$$2\log \gamma_A = -\sqrt{\mu} + B\mu \qquad (19)$$

Substituting in (18) and transposing,

$$\log K - B\mu = \log Kc - \sqrt{\mu} \qquad (20)$$

is obtained. Thus if we plot ($\log K_c - \sqrt{\mu}$), computed from the data in Table III, against μ, straight lines should be obtained in the more dilute solutions. Further, when $\mu = 0$, the right-hand member of Equation 20 equals log K. The plots of these quantities at the three temperatures are shown in Fig. 2. The plots are all drawn to the point at $\mu = 0$ corresponding 1.75×10^{-5} for K found by Harned and Owen. It is clear that the data at all three temperatures fall closely on these lines. We feel justified for the present in employing 1.75×10^{-5} for the dissociation constant at all three temperatures.

In Table IV are given the values of γ_A or $\sqrt{\gamma_H\gamma_{AC}/\gamma_{HAC}}$ in the solution of the two chlorides computed by Equation 17 from the values of m_H given in Table III.

It is apparent from these results that the activity coefficient of acetic acid decreases slightly with rising temperature at the higher ionic strengths. This is similar to the behavior of hydrochloric acid in the same salt solu-

TABLE IV

THE ACTIVITY COEFFICIENT OF ACETIC ACID IN THE SALT SOLUTIONS

MCl = KCl				MCl = NaCl			
M	γ_{A20}	γ_{A25}	γ_{A30}	M	γ_{A20}	γ_{A25}	γ_{A30}
0.05	0.798	0.796	0.796	0.05	0.787	0.785	0.185
.1	.790	.786	.786	.1	.769	.767	.766
.2	.776	.771	.770	.2	.747	.745	.742
.5	.758	.751	.747	.5	.727	.722	.717
I	.790	.779	.773	1	.756	,749	.741
1.5	.844	.834	.824	1.5	.815	.805	.798
2	.927	.911	.903	2	.884	871	.863
3	1084	1.067	1.057	3	1.051	1.033	1.017

tions. Further, this temperature effect is somewhat greater the higher the salt concentration. Finally, at a given ionic strength the activity coefficient is greater in potassium than in sodium chloride solutions, a fact observed by Harned and Robinson.[2] Indeed, at 25°, our electromotive force measurements closely check those of Harned and Robinson.

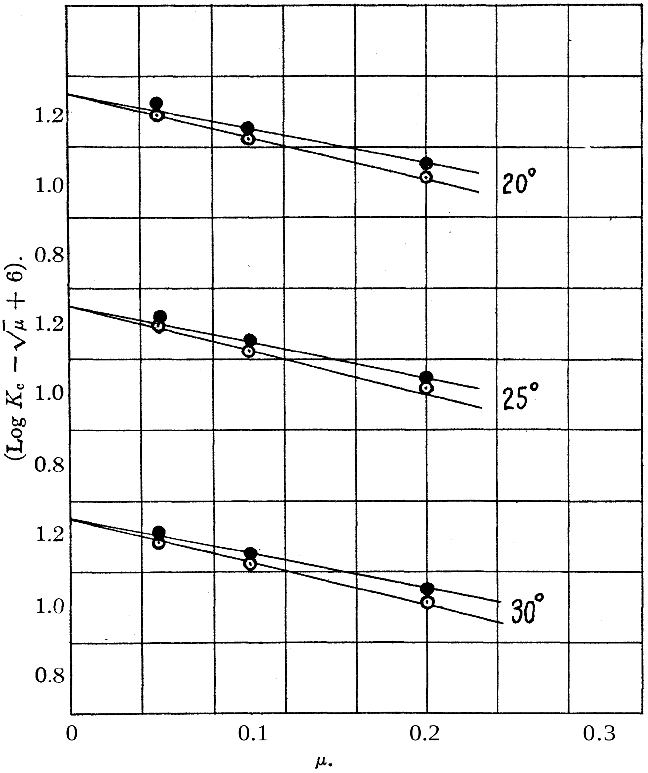

Fig. 2.—Graphical extrapolation to determine the dissociation constant of acetic acid at 20, 25 and 30°. O, KCl; ●, NaCl.

Calculation of the Electrical Heat Content Decrease.—We have made no calculations of the heat content decreases of the cell reaction from the electromotive force of the cells containing acetic acid. The only difference from the previous calculations would be that the hydrochloric acid is transferred from the salt solution containing some acetic acid. Moreover, since there is no convenient reference state upon which the calculations can be based, we cannot readily obtain the partial molal heat content.

It is a matter of some interest, however, to compute the excess or electrical partial heat content of hydrochloric acid from the results which we have so far derived.

According to theory, the partial free energy of an electrolyte may **be** divided into two parts as follows

$$\Delta\bar{F} = \Delta\bar{F}_c + \Delta\bar{F}_e \tag{21}$$

where

$$\left.\begin{aligned}\Delta\bar{F}_c &= RT \ln m, \text{ and}\\ \Delta\bar{F}_e &= RT \ln \gamma\end{aligned}\right\} \tag{22}$$

$\Delta\bar{F}_c$ is the contribution to the free energy due to the change in concentration, $\Delta\bar{F}_e$ is the contribution to the partial free energy caused by the electrostatic forces, and is denoted "the electrical free energy" or the excess free energy caused by the ionic atmosphere. Since γ is unity when m equals zero, $\Delta\bar{F}_e$ equals zero when m equals zero.

$\Delta\bar{F}_e$ may be computed readily, but we are more interested at present in the corresponding values of $\Delta\bar{H}_e$, or the excess heat content. The Gibbs–Helmholtz equation is

$$\frac{\mathrm{d}(\Delta\bar{F}_e/T)}{\mathrm{d}T} = \frac{\mathrm{d}(R \ln \gamma)}{\mathrm{d}T} = -\frac{\Delta\bar{H}_e}{T^2} \tag{23}$$

whence

$$(-\Delta\bar{H}_e) = 2.303RT^2\frac{\mathrm{d}\log\gamma}{\mathrm{d}T} = 2.303\,\frac{RT^2}{\gamma}\,\frac{\mathrm{d}\gamma}{\mathrm{d}T} = 2.303\,RT^2 A_{25} \tag{24}$$

The values of $\mathrm{d}\gamma/\mathrm{d}T$ have been determined in the following manner. The temperature variation of γ was computed by an empirical equation similar to Equation 1. The values of a_{25} thus obtained were plotted and

TABLE V

THE EXCESS HEAT CONTENT DECREASE OF HYDROCHLORIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS AT 25° IN CALORIES

	KCl		NaCl	
M	$(-\Delta\bar{H}_e)_{25}$	10^5A_{25}	$(-\Delta\bar{H}_e)_{25}$	10^5A_{25}
0.05	+40.6	−10.0	99.6	− 24.5
.1	65.0	− 16.0	143.1	− 35.2
.2	111.7	− 25.0	186.6	− 52.0
.5	160.0	− 41.8	335.1	− 82.4
1	243.1	− 59.8	490.8	−120.7
1.5	297.6	− 73.2	618.9	−152.2
2	342.3	− 84.2	701.4	−172.5
3	406.6	−100.0	827.5	−203.5

a smooth curve drawn through the points. From this curve A_{25} could be computed with considerable accuracy. The values of A_{25} and the decrease in the excess partial heat content, $-\Delta\overline{H}_e$, of the acid in the salt solutions computed by Equation 24 are given in Table V. In Fig. 3 these values of $(-\Delta\overline{H}_e)_{25}$ are plotted against $m^{1/2}$, and it is seen that the points fall on straight fines. Similar calculations for acetic acid were made but since at present the results appear to have no particular value, they have not been included.

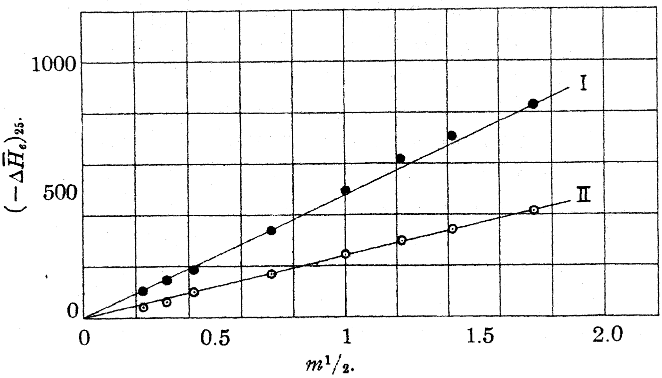

Fig. 3.—The excess relative heat content of hydrochloric acid in potassium and sodium chloride solutions. ●, HCl in NaCl; ○, HCl in KCl.

Summary

1. Measurements of the cells

H_2 | HCl (0.01), MCl (m) | AgCl | Ag, and
H_2 | HAc (0.2), MCl (m) | AgCl | Ag

have been obtained at 20, 25 and 30°. Potassium and sodium chlorides were the salts employed.

2. The activity coefficients of hydrochloric acid in the salt solutions at the three temperatures have been computed.

3. The hydrogen-ion concentrations of the acetic acid salt solutions have been computed.

4. The dissociation constant of acetic acid was found to vary very little if at all through the temperature range of from 20 to 30°.

5. The ionic activity coefficient of acetic acid in sodium and potassium chloride solutions at the three temperatures were computed.

6. The excess or electrical contribution to partial molal heat content of hydrochloric acid in the chloride solutions was computed and found as a first approximation to be proportional to the square root of the total molality.

New Haven, Connecticut

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ROYAL VETERINARY AND AGRICULTURAL COLLEGE]

THE VELOCITY OF DECOMPOSITION OF THE CARBONATO-TETRAMMINE-COBALTIC ION AND ITS DEPENDENCE ON THE HYDROGEN-ION CONCENTRATION

BY KAI JULIUS PEDERSEN

RECEIVED JULY 16, 1930 PUBLISHED JANUARY 12, 1931

During the last few years new light has been thrown on the field of hydrogen- and hydroxyl-ion catalysis. The recent progress is to a great extent due to the work of Bronsted and his collaborators.[1] Bronsted's views on catalysis are intimately connected with his theory of acids and bases.[2] According to this theory, any substance, whether it is a neutral molecule or an ion, is called an acid, if it has a tendency to split off protons, and a base, if it tends to add on protons. Thus if $A \rightleftharpoons B + H^+$, A is an acid and B the corresponding base. In Bronsted's theory of general acid and basic catalysis, catalytic effects are attributed not only to the hydrogen ion and to the hydroxyl ion, but to all substances which are sufficiently strong acids and bases according to the new definition. The magnitude of the catalytic effect increases with increasing acid or basic strength of the catalyst. The existence of general acid or basic catalysis has been experimentally established in a number of cases.[1] However, this fact does not exclude the possibility of cases of specific hydrogen or hydroxyl ion catalysis where only hydrogen or hydroxyl ions but not acids or bases in general are catalysts. The reaction

$$[Co(NH_3)_4(H_2O)(NO_3)]^{++} + H_2O \longrightarrow [Co(NH_3)_4(H_2O)_2]^{+++} + NO_3^-$$

examined by Bronsted[3] may be considered as being a case of specific hydroxyl-ion catalysis.

Let us consider the scheme[3a]

$$R + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RH^+ + A^- \qquad (1)$$

$$RH^+ \xrightarrow{k_2} \qquad (2)$$

k_1, k_{-1} and k_2 are velocity constants. We consider the two special limiting cases

(a) $k_2 \gg k_1 \times c_{HA}$, $k_2 \gg k_{-1} \times c_{A^-}$. Reaction 1 from left to right determines the velocity of the total reaction. Practically all the molecules RH^+ react according to (2) before they get time to react with A^- and form $R + HA$ again. We have general acid catalysis.

(b) $k_{-1} \times c_{A^-} \gg k_1 \times c_{HA} \gg k_2$. Equilibrium 1 is maintained all

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[1] **J. N. Bronsted,** *Trans. Faraday Soc.*, 24, 630 (1928).

[2] **J. N. Bronsted, J.** *Phys. Chem.*, *30*, *777* (*1926*).

[3] *J.* **N. Bronsted,** *Z. physik. Chem.*, 122, *383* (1926).

[3a] Cf. **Skrabal** *Trans. Faraday Soc.*, *24*, 687 (1928).

the time. The concentration of RH+ is small compared with that of R c_{RH^+} and consequently the velocities are only dependent on the hydrogen-ion concentration, when the salt effect is neglected. In this case we have *specific hydrogen-ion catalysis.*

These are special limiting cases. Reactions where both the velocities of (1) as well as that of (2) affect the velocity of the total reaction are quite possible, although their existence has not yet been experimentally established.

The present work was started as a contribution to the study of these different kinds of catalysis.

Carbonato–tetrammine–cobaltic salts have been prepared by S. M. Jörgensen.[4] He found that they split off carbon dioxide almost instantaneously with cold dilute hydrochloric acid. With very dilute acid (< 1 N) only diaquo-tetrammine salt is obtained

$$[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+ + 2\text{H}^+ + \text{H}_2\text{O} \longrightarrow [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{+++} + \text{CO}_2 \qquad (3)$$

With more concentrated hydrochloric acid some chloro-ayuo-tetrammine salt is also formed.

In the present work the kinetics of Reaction **3** have been studied at 25° and at different hydrogen-ion concentrations. The experiments fall into 4 series: (1) in glycolate buffer solutions with the total salt concentration 0.11 N. (The hydrogen-ion concentration was here varied within the ratio of 1 to 10); (2) in glycolate buffers with the salt concentration 0.21 N; **(3)** in acetate buffers with the salt concentration 0.98 N; (4) in acetate buffers with the salt concentration 0.11 N.

It will be shown that the velocity may be expressed as the sum of two velocities, one being independent of the hydrogen-ion concentration, the other being proportional to the hydrogen-ion concentration:

$$\frac{\text{d}x}{\text{d}t} = (k_0' + k_1' \times c_{\text{H}^+})(c-x) \qquad (4)$$

where c is the initial concentration and $c - x$ the concentration at the time t of the carbonato-tetrammine-cobaltic salt; k_0' and k_1' are constants.

This simple relationship only holds when the carbon dioxide pressure is small or the hydrogen-ion concentration comparatively great. However, the following treatment will be based on Equation 4, and we shall see how well the experiments agree with it.

The Apparatus

The rate of Reaction **3** was followed by measuring the pressure of the carbon dioxide above the solution during the reaction. For this purpose a modification of Bronsted's shaking apparatus[5] was used. In its original form it could be used only in a narrow temperature interval, namely at and a little below room temperature, because a part

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[4] S. M. Jorgensen, *Z. anorg. Chem.*, 2,279 (1892).

[5] Brönsted and King, THIS JOURNAL, 47,2523 (1925).

of the apparatus is above the water of the thermostat. Above room temperature water distils from the solution in the flask to the top of the apparatus, and the condensed water is apt to run down into the glass spring.

In its new form the apparatus is completely under water except one end of the pressure gage (Fig. 1). The reaction flask A with a capacity of 200 cc. is connected with the mercury manometer C through the elastic glass capillary B, which allows a horizontal shaking of the flask A to prevent supersaturation. The apparatus is made in two separate parts. One piece is the part which is in the thermostat, ending in the horizontal tube which goes through the wall of the thermostat. The second piece is the tube C which is originally open at the top. The two pieces are put in their positions and fused together. Mercury is poured into C through the opening at the top. The apparatus is evacuated to a low pressure simultaneously through C and the tap D. C is sealed off above the spherical part, and the apparatus is ready for use. F is an arrangement to hold and, when desired, to drop a small platinum bucket into the solution in the flask A. It consists of a ground slip-on stopper which has inside a little glass rod ending in a platinum hook. Before the start of an experiment the bucket containing the substance for the reaction is suspended on the hook. When the stopper is turned through 180° the bucket is released and drops into the flask When an experiment was to be done so much water was removed from the thermostat through the tap G that the opening of the flask A was above the surface. The buffer solution (in each experiment 100 cc.) was poured into the flask. The bucket with the carbonato-tetrammine-cobaltic salt (about 0.001 mole in each experiment) was suspended on the hook The apparatus was closed by means of the ground slip-on stopper E, and the water which had been removed from the thermostat was poured back The shaker was started, and the apparatus was evacuated through the tap D. The reaction was started when the substance was dropped into the solution. In all the experiments the temperature was kept constant at 84.95 ± 0.01°.

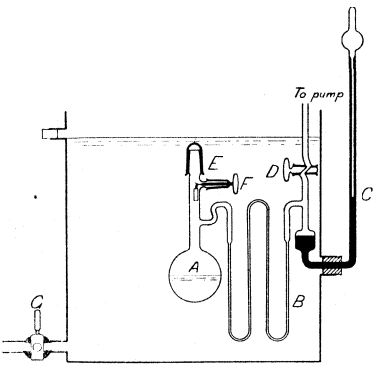

Fig. 1.

Calculation of the Velocity Constants.—We use the following symbols.

The stoichiometrical initial concentrations of the buffer solution	
Acid HA (glycolic or acetic acid)	*a* molar
Sodium salt NaA (glycolate or acetate)	b molar
Initial concentration of carbonato-tetrammine ion	c molar
Its concentration at the time *t*	$c - x$ molar
Concentration dissociation constant of the acid of the buffer solution	K
Activity dissociation constant of the same	K_0

Ratio between the concentrations of undissociated acid (glycolic or acetic) and ion (glycolate or acetate) at the time *t*

$$h = \frac{c_{\mathrm{HA}}}{c_{\mathrm{A}^-}} = \frac{c_{\mathrm{H}^+}}{K}$$

At the time $t = 0$ we set $h = h_0$, at the time $t = \infty$ we set $h = h_\infty$. $^1/_2\ (h_0 + h_\infty) = h_m$.

The equilibrium constant for the reaction

$$[\mathrm{Co(NH_3)_4(H_2O)_2}]^{+++} + A^- \rightleftarrows [\mathrm{Co(NH_3)_4(H_2O)(OH)}]^{++} + \mathrm{HA} \qquad \mathrm{L}$$

We now rewrite Equation 4 as follows

$$\frac{dx}{dt} = (k_0' + k_1' \times c_{\mathrm{H}^+})(c - x) = (k_0' + k_1' \times K \times h)(c - x) \tag{5}$$

Both k_1' and K vary with the salt concentration, but in a series of experiments where the total salt concentration is kept constant while h varies, k_1', K and accordingly also the product $k_1' \times K$ may be considered as constants. We must, however, take into account that the composition of the buffer solution, expressed by h and determining c_{H^+}, alters during the reaction according to (3). Further, the reaction product $[\mathrm{Co(NH_3)_4(H_2O)_2}]^{+++}$ is a weak acid which has also some effect on h. We have

$$h = \frac{a - hK - 2x + \frac{L}{L + h}x}{b + hK + 2x - \frac{L}{L + h}x}$$

Using the abbreviations

$$A = \frac{a - h_0K}{2 - \frac{(h_0 - h_\infty)K}{c} - \frac{L}{L + h_m}} \tag{6}$$

$$B = \frac{b + h_0K}{2 - \frac{(h_0 - h_\infty)K}{c} - \frac{L}{L + h_m}} \tag{7}$$

we have to a sufficient approximation $h = (A - x)/(B + x)$. In particular $h_0 = A/B$ and $h_\infty = (A - c)/(B + c)$. In order to calculate A and B we must know approximate values of K, L, h_0 and h_∞.

We can now write the differential Equation 5 in the following form

$$\frac{dx}{dt} = \left(k_0' + k_1'K\frac{A - x}{B + x}\right)(c - x)$$

Integrating and noting that $x = 0$ when $t = 0$ we get

$$kt = \log\frac{c}{c - x} - \frac{1 + h_\infty}{1 - f}\log\frac{fB + A}{fB + A - (1 - f)x} \tag{8}$$

where $k = k_0 + K\,k_1h_\infty$, $k_0 = 0.4343\,k_0'$, $k_1 = 0.4343\,k_1'$ and $f = k_0/Kk_1$.

The difference between the manometer readings p_∞ at the time $t = \infty$ and p at the time t is called $P = p_\infty - p$. P is proportional to $c - x$. $P = \varphi\,(c - x)$. We find the constant φ according to $\varphi = P_0/c$. Formula 8 is now transformed into

$$kt = \log\frac{P_0}{P} - \left(1 + \frac{f + h_\infty}{1 - f}\right)\log\frac{\frac{f + h_\infty}{1 - f}(B + c)\varphi + P_0}{\frac{f + h_\infty}{1 - f}(B + c)\varphi + P} \equiv \psi\,(P) \tag{9}$$

The second term of $\psi\,(P)$ expresses the effect of the change in hydrogen-ion concentration during the reaction. Generally this term is small compared with $\log P_0/P$.

The ratio f being unknown, we provisionally plot $\log\,(P_0/P)$ against t for a whole series of experiments with constant total salt concentration but with varying h,. In this way we find an approximate value for k for each experiment. We now plot these approximate values against h,. The points fall fairly well on a straight line determining according to the equation $k = k_0 + K \times k_1 \times h_\infty$ approximate values of k_0 and $K \times k_1$. From these we find an approximate value of f which we use in (9). We now plot $\psi(P)$, calculated by means of the approximate value for f against t, and find better values for k_0, $K \times k_1$ and f. By successive repetitions we continue until a repetition gives the same values again.

For the calculation of A and B, (6) and (7), it is necessary to know K and L. Fortunately they enter the expressions only in small correction terms; consequently only rough values of K and L are necessary. The activity dissociation constants found by conductivity at 25° are for glycolic acid[6] $K_0 = 1.54 \times 10^{-4}$ and for acetic acid $K_0 = 1.81 \times 10^{-5}$ (recalculated from the measurements of Kendall[7] by C. W. Davies).[8] With sufficient approximation except for the 1 N acetate, we may use the formula $-\log K = -\log K_0 - \sqrt{\mu} + \mu$, where μ is the ionic strength. We thus get for the glycolate buffer, salt concentration 0.11 N, $K = 2.6 \times 10^{-4}$, and at the salt concentration 0.21 N, $K = 3 \times 10^{-4}$. For the acetate buffer, salt concentration 0.11 N, we get $K = 3.0\ X\ 10^{-5}$. Bronsted and Volqvartz[9] have determined the acid dissociation constant of the diaquo-tetrammine-cobaltic ion

$$[Co(NH_3)_4(H_2O)_2]^{+++} \rightleftharpoons [Co(NH_3)_4(H_2O)(OH)]^{++} + H^+$$

They find at 15°, $-\log K_{Aq.} = 5.21 + 2\sqrt{\mu} - \mu$. From this and their measurement at 20° $\sqrt{\mu} = 0.29$, $-\log K_{Aq.} = 5.52$, we find by extrapolation to 25°, $-\log K_{Aq} = 4.87 + \sqrt{\mu} - P$. By combining this with the K values for glycolic and acetic acid, we find rough values for L.

Glycolate buffers, salt concentration 0.11 N, L = 0.015
Glycolate buffers, salt concentration 0.21 N, L = 0.010
Acetate buffers, salt concentration 0.11 N, L = 0.13

In the acetate buffers with the salt concentration 0.98 N, the change in hydrogen-ion concentration during the reaction is so small that it is sufficient to use $A = a/2$ and $B = b/2$.

Preparation and Purification of the Substances

Carbonato–tetrammine–cobaltic sulfate $[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$ was prepared by the method of S. M. Jörgensen.[10] It was recrystallized from water and again dissolved and precipitated with alcohol. For some of the experiments the nitrate $[Co(NH_3)_4CO_3]NO_3 \cdot 0.5H_2O$ was used. My thanks are due to Professor Bronsted for a pure preparation of this salt.

[6] Boeseken and Kalshoven, *Rec. trav. chim.*, **37**, 130 (1918).

[7] Kendall, J. *Chem. Soc.*, **101**, 1275 (1912).

[8] Davies, J. *Phys. Chem.*, 29,973 (1925).

[9] Bronsted and Volqvartz, *Z. physik. Chem.*, **134**, 97 (1928).

[10] S. M. Jorgensen, Ref. 4, p. 281.

The glycolic acid was purified through the barium salt, which was recrystallized twice from water. To a warm solution of the pure barium glycolate was added a small excess of 4 *N* sulfuric acid. When there is no excess of sulfuric acid the barium sulfate forms a colloidal solution. However, a small excess of the acid makes it easy to filter the barium sulfate from the solution. Afterward all the sulfuric acid could be removed by a little barium glycolate and a new filtration. The filtrate gave a hardly visible reaction with barium ions. The concentration of glycolic acid was determined by titration.

Acetic acid (Merck "Zur Analyse") was used without purification.

The buffer solutions were prepared from the solutions of the acids and sodium hydroxide solution, made of sodium hydroxide Merck "puriss. e natrio." The various glycolate buffer solutions were prepared from a standard solution by adding various amounts of hydrochloric acid and diluting.

The Experimental Data

The experimental results are given in Tables I–IV and Figs. 2–4. Experiments 1–10 and 14–16 were done with carbonato-tetrammine-cobaltic sulfate, while the nitrate was used for Experiments 11–13. In Figs. 2–3 are plotted the values of ψ (P) for each reading against the time *t* in minutes. In the experiments on glycolate (Nos. 1–10, Tables I–II, Fig. 2) the points fall well on a straight line for the greatest part of each reaction. However, at the end the velocity is always smaller than that corresponding to the

TABLE I

THE DECOMPOSITION OF THE CARBONATO–TETRAMMINE–COBALTIC ION

Glycolate buffers; total salt concentration, 0.11 N; temp., 24.95°

No.	*c*	a	*b*	NaCl	h_0	h_∞	k (found)	k (calcd.)
1	0.01000	0.05106	0.09991	0.00000	0.5091	0.2624	0.00455	0.00449
2	.00979	.06617	.08480	.01511	0.7761	.4481	.00578	.00580
3	.00978	.08128	.06969	.03022	1.157	.6912	.00757	.00750
4	.00990	.08883	.06214	.03777	1.415	.8400	.00848	.00855
5	.00969	.09638	.05459	.04532	1.743	1.037	.00982	.00993
6	.00953	.11148	.03949	.06042	2.754	1.563	.01372	.01362

k = 0.00265 + 0.00702 h_∞ (min.$^{-1}$, decad. logs), or k = 0.00265 + 46.6 K_0h_∞ (min.$^{-1}$, decad. logs).

TABLE II

THE DECOMPOSITION OF THE CARBONATO–TETRAMMINE–COBALTIC ION

Glycolate buffers; total salt concentration, 0.21 *N*; temp., 24.95°

No.	c	a	b	NaCl	h_0	h_∞	*k* (found)	k (calcd.)
7	0.00973	0.1021	0.1998	0.0000	0.5103	0.3779	0.00606	0.00607
8	.00976	.1625	.1394	.0604	1.161	.8983	.01061	.01066
9	.00971	.1990	.1029	.0969	1.920	1.462	.01564	.01560
10	.00988	.0813	.0697	.1302	1.156	0.6861	.00859	(.00895)

k = 0.00275 + 0.00879 h_∞ (min.$^{-1}$, decad. logs), or k = 0.00275 + 57.1 K_0h_∞ (min.$^{-1}$, decad. logs).

straight line. This drop in velocity is the more pronounced the smaller the hydrogen-ion concentration. The small lines crossing the curves in each experiment show where the reaction is half completed. Owing to this drop in velocity it was always necessary to wait for several days for the infinity reading. In Tables I–II are given the k values determined by the slopes of the straight lines. By plotting k against h_∞ we find k_0 and $K \times k_1$ for each of the two series of experiments. At the bottom of each table are given the values of k_0 and $K \times k_1$ determined in this way.

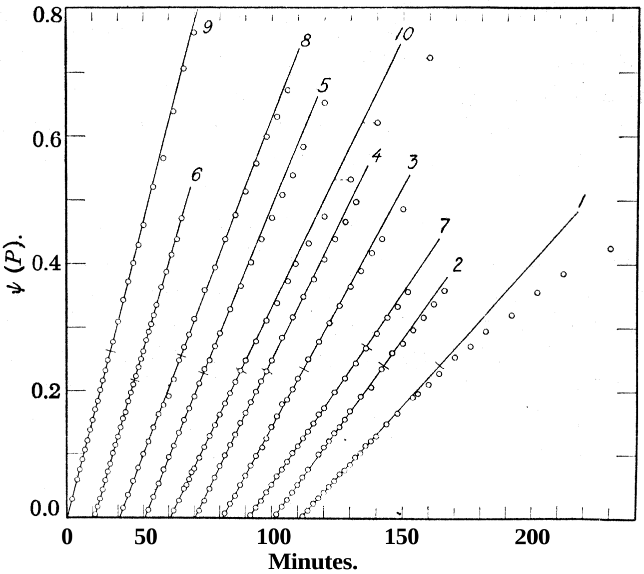

Fig. 2.—The rate of decomposition of the carbonato-tetrammine-cobaltic ion in glycolate buffer solution (Tables I–II).

The last column of the tables gives k calculated from these values. There is a good agreement between k (found) and k (calcd.). All the experiments in glycolate buffer solutions gave practically the same amount of carbon dioxide per equivalent of carbonato salt. Therefore, the reaction may be considered as being practically complete.

TABLE III

THE DECOMPOSITION OF THE CARBONATO-TETRAMMINE-COBALTIC ION

Acetate buffers; total salt concentration 0.98 *N*; temp., 24.95°

No.	*c*	*a*	*b*	h_0	h_∞	*k* (found)	*k* (calcd.)
11	0.00987	1.008	0.974	1.035	0.994	0.00466	0.00466
12	.00957	1.344	.974	1.380	1.332	.00526	.00530
13	.01075	2.013	.974	2.066	2.000	.00660	.00656

$k = 0.00278 + 0.00189\, h_\infty$ (min.$^{-1}$, decad. logs), or $k = 0.00278 + 104\, K_0 \times h_\infty$ (min.$^{-1}$, decad. logs).

TABLE IV

THE DECOMPOSITION OF THE CARBONATO-TETRAMMINE-COBALTIC ION

Acetate buffers; total salt concentration, 0.11 *N*; temp., 24.95°

(TABLE IVa)

No.	c	a	b	ha	h_∞	k (calcd.)
14	0.00982	0.0939	0.1000	0.939	0.650	0.00519
15	.00998	.1756	.1000	1.766	1.32	.00374
16	.00766	.0939	.1000	0.941	0.718	.00325

(TABLE IVb)

No.	$p\text{CO}_2(t = 0)$	$p\text{HCO}_3^-(t = 0)$	$p\text{Co}(t = 0)$	$p\text{CO}_2(t = \infty)$	$p\text{HCO}_3^-(t = \infty)$	$p\text{Co}(t = \infty)$	α	$M \times 10^{-2}$	α (calcd.)
14	0.00	0.00	7.23	6.91	0.06	0.26	0.964	4.4	0.968
15	.00	.00	7.59	7.49	.03	.07	.991	4.7	.991
16	19.87	.11	5.63	24.94	.18	.49	.913	5.1	.910

$M \times 10^{-2} = 4.9.$

In the acetate buffer solutions with the salt concentration 0.11 *N* (Nos. 14–16, Table IV and Fig. 3), the drop in velocity is so great that no straight line can be drawn. The drop is especially great in Expt. 16. Here the hydrogen-ion concentration is about the same as in Expt. 14, but some carbon dioxide was in the apparatus at the start of the experiment. In order to compare the experiments with those in glycolate at the same salt con-

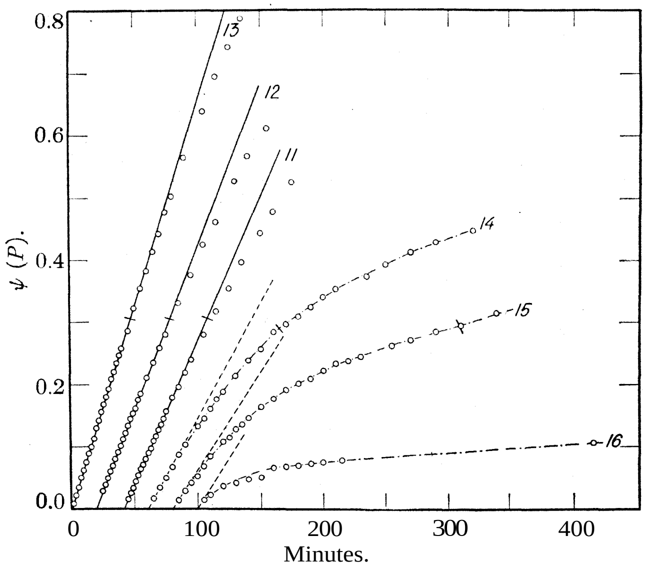

Fig. 3.—The rate of decomposition of the carbonato-tetrammine-cobaltic ion in acetate buffer solutions (Tables III–IV).

centration, where Equation 4 holds, we write the velocity constant k = 0.00265 + 45.6 K_0h_∞. We introduce the activity dissociation constant for acetic acid instead of that for glycolic acid and calculate k values for the different values of *h*,. In this way we get the k (calcd.) given in the seventh column of Table IVa. The dotted lines in Fig. **3** are drawn with the slopes k (calcd.). They fit quite well as tangents for $t = 0$. The total amount of carbon dioxide evolved in these experiments is a little smaller per equivalent carbonato salt than in the glycolate buffers. Owing to the low hydrogen-ion concentration a little carbon dioxide will be bound as bicarbonate in the solution. However, as will be shown in the following calculation, this is far from being enough to explain the decrease. Consequently, it would seem that the reaction is balanced. In order to show this we try to calculate the equilibrium constant.

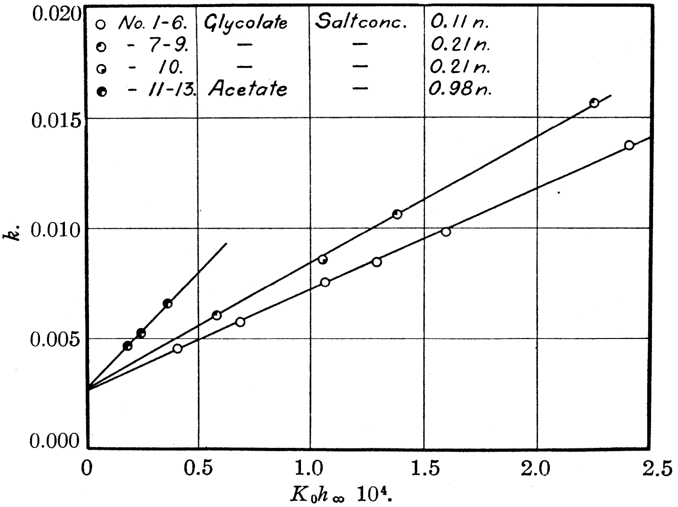

Fig. 4.—The dependence between the velocity constant and the hydrogen-ion concentration.

We denote by p_{CO_2} the carbon dioxide pressure in cm. of mercury. $p_{HCO_3^-}$ and p_{Co} are the additional pressures which would have been measured if the carbon dioxide were completely liberated from the bicarbonate and the complex cobaltic salt, respectively. Our first object is to calculate $p_{Co(t = \infty)}$. We have

$$p_{Co(t = \infty)} = p_{CO_2(t = 0)} + p_{HCO_3^-(t = 0)} + p_{Co(t = 0)} - p_{CO_2(t = \infty)} - p_{HCO_3^-(t = \infty)} \quad (10)$$

In Experiments 14 and 15, $p_{CO_2(t = 0)} = 0$ and $p_{CO_2(t = \infty)} = P_0$. In 16, where carbon dioxide is present at the start, $p_{CO_2(t = 0)}$ and $p_{CO_2(t = \infty)}$ are found by subtracting from the readings at $t = 0$ and $t = \infty$ the reading at $t = 0$ in Expt. 14, which was done in the same apparatus and with the same composition of the solution as in Expt. 16. $p_{Co(t = 0)} = \varphi c$. For

φ is used the value found in the glycolate experiments; in Expts. 14 and 16, $\varphi = 736$; in Expt. 15, which was done in another apparatus, $\varphi = 761$. It remains to calculate $p_{HCO_3^-}$ at the times 0 and ∞. The apparent first dissociation constant of carbonic acid is at 25° 3.12×10^{-7}, found by conductivity by Wilke.[11] The ratio between the constants of carbonic acid and acetic acid is $3.12 \times 10^{-7}/1.81 \times 10^{-5} = 0.0172$. Consequently we have

$$c_{HCO_3^-} = \frac{0.0172}{h}(c_{CO_2} + c_{H_2CO_3}),\ \textit{or}$$

$$p_{HCO_3^-} = \frac{0.0172}{h}\varphi\,(c_{CO_2} + c_{H_2CO_3})$$

$$c_{CO_2} + c_{H_2CO_3} = 0.759\,\frac{p_{CO_2} \times 273}{76 \times 22.4 \times 298}$$

0.759 is the Bunsen absorption coefficient for carbon dioxide in water.[12] We thus get

$$p_{HCO_3^-} = \frac{0.0172 \times 273 \times 0.759}{76 \times 22.4 \times 298}\,\frac{\varphi \times p_{CO_2}}{h} = 7.03 \times 10^{-6}\,\frac{\varphi\, p_{CO_2}}{h}$$

Finally, we find $p_{Co(t=\infty)}$ by Equation 10. The p values are given in Table IVb. We now calculate the degree of decomposition a of the carbonato salt at equilibrium for the three experiments.

$$1 - \alpha = \frac{p_{Co(t=\infty)}}{p_{Co(t=0)}}$$

a is given in the eighth column of Table IVb. In the ninth column is given the equilibrium constant expressed by

$$M = \frac{\alpha \times p_{CO_2(t=\infty)}}{(1-\alpha) \times h^2_\infty}$$

The values are constant within the limits of the experimental error. This is seen from the last column, where we have calculated α using the value $M = 4.0 \times 10^2$. In spite of the good constancy, too much weight must not be laid on this result. It is difficult to understand the great drop in velocity without assuming that the equilibrium is reached through two consecutive balanced reactions. If there is an appreciable amount of the intermediate substance present at equilibrium, the above calculation is not unobjectionable. Another objection is that possibly a formation of acetato complexes

$$[Co(NH_3)_4(H_2O)_2]^{+++} + CH_3COO^- \rightleftharpoons [Co(NH_3)_4(H_2O)(CH_3COO)]^{++} + H_2O$$

may take place. However, rough colorimetric test-tube experiments with different acetate solutions up to 1 N acetate left for several days did not support the assumption that acetato complexes were formed.

In the experiments in the more concentrated acetate buffers (salt concentration 0.98 N) the decomposition was found to be practically complete,

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[11] **Wilke,** Z. anorg. Chem., 119,365 (1921).

[12] **Chr.** Bohr, *Wied.* Ann., 68,504 (1899).

and the simple equation (4) was found to hold for the greater part of the reaction (Table III and Fig. **3,** Expts. 11–13).

Discussion

We first consider the experiments where the fundamental equation (4) holds for a considerable part of the reaction (Expts. 1–13). By means of the equation $k = k_0 + k_1Kh_\infty$, we found for each series of experiments by plotting k against h_∞ the constants k_0 and $K \times k_1$. In order to facilitate a comparison of the experiments in acetate and glycolate buffers we write the equation in the form $k = k_0 + (k_1F) \times (K_0h_\infty)$. K_0 is the activity dissociation constant and F a factor expressing the salt effect on K. $F = f_{HA}/f_{H^+}f_{A^-}$, where f_{HA}, f_{H^+} and f_{A^-} are activity coefficients. While K varies with the salt concentration and is not known with sufficient accuracy, K_0 is constant and known with good accuracy. In Fig. 4 k is plotted against K_0h_∞. For each of the three series of experiments the points fall on a straight line. The slopes determine k_1F, their intercepts on the ordinate axis k_0. It is seen that all three series give almost the same value of k_0 while k_1F increases with increasing salt concentration. At the bottom of Tables I–III the equations of the straight lines are given.

No general acid catalysis was found. It is true that an increase in the concentrations of the buffer substances causes an increase in velocity (compare Expts. 1–6 with 7–9). But the same increase is produced by adding sodium chloride to the same total salt concentration (Expt. 10). Consequently the increase may be explained as neutral salt effect. Neither is it possible to detect any general acid catalysis by a comparison with each other of the data of any of the two series (Expts. 1–6 and 7–9). If we did assume an effect of the undissociated glycolic acid, we should have

$$\begin{aligned} k &= k_0 + (k_1F)(K_0h_\infty) + k_{HA} \times c_{HA} \\ &= k_0 + \left[(k_1F) + \frac{k_{HA}}{K_0}c_{A^-}\right] K_0h_\infty \end{aligned}$$

Consequently we should get no straight lines in Fig. 4 for the experiments in glycolate, where the concentration of glycolate is varied. If we assume that the values found for k_1F are constant within each series within an accuracy of 2%, we have

(Expts. 1 and 6) $$1.02\left(k_1F + \frac{k_{HA}}{K_0}0.04\right) > k_1F + \frac{k_{HA}}{K_0}0.10$$

that is, $k_{AH} < 5 \times 10^{-5}\, k_1F$

(Expts. 7 and 9) $$1.02\left(k_1F + \frac{k_{HA}}{K_0}0.10\right) > k_1F + \frac{k_{HA}}{K_0}0.20$$

that is, $k_{AH} < 3 \times 10^{-5}\, k_1F$

In order to find how great an effect of the undissociated glycolic acid we should reasonably expect if there were general acid catalysis, we use a method of calculation put forward by Brönsted.[13] In reactions with

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[13] **J. N. Bronsted,** *Trans. Faraday* Soc., *24, 639 (1928).*

general acid catalysis the part of the reaction which is independent of the acid concentration, the so-called "spontaneous" reaction, may be considered as a catalysis of the acid H_2O. Bronsted gives the following formula for a very rough calculation of the effect of an acid if the effects of two other acids (*e.* g., H_3O^+ and H_2O) are known. The dissociation constants are denoted by K_a, K_b and K_c, the corresponding catalytic coefficients by k_a, k_b and k_c.

$$\log \frac{k_a}{k_b} \Big/ \log \frac{k_c}{k_b} = \log \frac{K_a}{K_b} \Big/ \log \frac{K_c}{K_b}$$

Acid (a), glycolic acid; $K_a = 1.5 \times 10^{-4}$; $k_a = k_{HA}$
Acid (b), H_3O^+; $K_b = 56$; k_b is roughly $k_1F = 5 \times 10$
Acid (c), H_2O; $K_c = (1.05 \times 10^{-14})/56 = 1.9 \times 10^{-16}$; $k_c = 0.0027/56 = 5 \times 10^{-5}$

We find $k_{HA} = 1.3 \times 10^{-2} \times k_1F$. This value is some hundred times greater than the greatest value $k_{HA} = 3 \times 10^{-5}\ k_1F$ which is reconcilable with the experiments.

As a result of this we may say that the rate of reaction is determined only by the hydrogen-ion concentration and a salt effect. The reaction may be considered as the sum of two simultaneous reactions, one being independent of the hydrogen-ion concentration, the other being catalyzed by hydrogen ions. The salt effect is in agreement with Bronsted's theory of kinetic salt effect,[14] according to which a reaction between an ion and an uncharged molecule in dilute solution is almost independent of the salt concentration, while an addition of salt accelerates a reaction between two ions with charges of the same sign and retards a reaction between ions of opposite sign. Consequently k_0 should be only slightly salt sensitive, while k_1 should increase with the salt concentration. Also the factor F should increase with increasing salt concentration In agreement we found almost the same k_0 at all salt concentrations, while k_1F showed a great increase with increasing salt concentration (Fig. 4).

As seen from Figs. 2 and 3 the simple formula (4) holds the better the greater the hydrogen-ion concentration and the smaller the carbon dioxide pressure. In Expts. 14 and 15 and especially 16, where extra carbon dioxide has been added, it fails completely. The reaction is balanced, but the drop in velocity is much greater than can be explained from the assumption that the velocity is determined by a single balanced reaction. A probable explanation seems to be the assumption of consecutive balanced reactions. However, we shall here refrain from suggesting a mechanism owing to the complicated nature of the calculations necessary to test it.

In conclusion the author wishes to thank the Carlsberg Foundation for a grant which has defrayed the expenses of the apparatus, and to express his great indebtedness to Professor Bjerrum for helpful criticism and valuable suggestions.

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[14] J. N. Brönsted, *Z. physik. Chem.*, *102*, 169 (1922); *Trans. Faraday Soc.*, *14*, 630 (1928).

Summary

The kinetics of the decomposition of the carbonato-tetrammine-cobaltic ion

$$[Co(NH_3)_4CO_3]^+ + 2H^+ + H_2O \rightleftharpoons [Co(NH_3)_4(H_2O)_2]^{+++} + CO_2$$

have been studied in glycolate and acetate buffer solutions at 25° and at different salt concentrations.

In the glycolate buffers the decomposition was practically complete. In some acetate buffers it could be shown that the reaction is balanced.

When the carbon dioxide pressure is low and the hydrogen-ion concentration not too small, the velocity may be expressed as the sum of two terms, one being independent of the hydrogen-ion concentration, the other being proportional to the hydrogen-ion concentration. No general acid catalysis was found.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE STATE UNIVERSITY OF IOWA]

SOLUBILITIES IN HYDROGEN FLUORIDE

BY P. A. BOND AND V. M. STOWE

RECEIVED JULY 28, 1930 PUBLISHED JANUARY 12, 1931

Solubility relations in non-aqueous inorganic systems have received attention in this Laboratory during several years. Sulfur monochloride, liquid nitrogen tetroxide, thionyl chloride and liquid sulfur dioxide have been employed as solvents.

As one branch of the general problem of solubilities in non-aqueous inorganic systems, the authors set out to develop a technique for the use of liquid anhydrous hydrogen fluoride as a solvent, and to determine some solubilities in this medium. Liquid hydrogen fluoride was chosen for this investigation because of its unusual properties.

The anomalous boiling point of liquid hydrogen fluoride indicates that it is an associated liquid. The anomaly is apparent if one compares the boiling points of the series HI (–35.7°), HBr (–68.7°), HCl (–83.1°) and HF (+19.0°). Water and ammonia show similar anomalous boiling points when compared with the appropriate series. The vapor pressure data of Simons[1] were examined by the use of Hildebrand's modification of the Trouton rule.[2] The value of the "constant" so determined is about the average of those for normal liquids.

The chemical relationships for hydrogen fluoride indicated that it would prove to be a good solvent. Polar liquids such as ammonia, water and,

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[1] J. Simons, THIS JOURNAL, 46, 2179 (1924).

[2] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, p. 89.

to a less extent, alcohol, frequently form addition compounds with solutes. This appeared to be true also in the case of hydrofluoric acid.

Finally, the qualitative results of Gore[3] and Franklin[4] indicated that hydrogen fluoride is a vigorous reagent and a good solvent. The authors believe, however, that many of the solubilities in hydrogen fluoride previously reported were preceded by chemical reaction.

Recent publication by Cadenbach[5] is quite in line with this statement. His results, while qualitative, or where quantitative, expressed in terms of molar solutions, are in quite close agreement with the results shown below.

Preparation of Hydrogen Fluoride

The liquid anhydrous hydrogen fluoride was prepared essentially according to the method of Gore,[3] *i. e.*, by the distillation of dry potassium hydrogen fluoride, KHF_2. For the preliminary work Baker and Adamson "C. P." potassium bifluoride was fused, electrolyzed by a direct current of 18 volts until arcing was no longer seen at the carbon pole, and the product was distilled from a platinum still described below. Later the potassium fluoride resulting from this distillation was treated with aqueous hydrogen fluoride, evaporated, fused and electrolyzed as above.

The acid salt is reported to be non-hygroscopic. However, electrolysis of the fused salt as carried out served to remove any trace of water which might have been present. The salt was then always preserved in a desiccator. The fused salt was poured into a clean platinum still which had been carefully dried. The still was then suspended by a nichrome wire so that the condensing tube was engaged. Heat was applied by means of a specially designed electric heating unit which supplied the heat in a ring about the still, and which could be moved up and down the still as desired. In this way the heat was applied above the acid salt and any frothing was checked by contact with the hot part of the still above. A light red heat was used. After three hours most of the acid had been distilled off from the salt. The vapor passed through a platinum tube 40 cm. long. This was surrounded by a water jacket which served to cool the gas to room temperature. The platinum tube was sealed with sulfur onto a spiral monel metal tube about three meters long and about 8 mm. in diameter. In the spiral, which was packed in an ice and salt freezing mixture, the hydrogen fluoride was condensed to a liquid. The liquid was collected directly in the solubility apparatus, which was sealed onto the still each time with ceresin wax, thus exposing only a very small amount of wax and that to the vapor only. Air pressure was equalized through a drying tube. The hydrogen fluoride obtained was clear, limpid and colorless. It carried less than 0.2% of non-volatile solid as shown by seven determinations made on amounts of hydrogen fluoride ranging from approximately 8 to 14 g.

Procedure for Determining Solubility.—The "bomb," or solubility apparatus, which was specially designed for this work, comprised the upper chamber (A, see Fig. 1) and the lower chamber (B). The piece (E) served as a partition and also formed the seat of the valve as shown. (E) was held in place by the union (D). Soft gaskets of 24 carat gold maintained an air-

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[3] Gore, *Phil. Trans.*, 159, *183* (1869).

[4] Franklin, *Z. anorg. Chem.*, *46*, 2 (1905).

[5] Karl Fredenhagen and Gustav Cadenbach, *Z. physik. Chem.*, Abt. A, *146*, 245 (1930).

tight joint. The valve stem was packed with ceresin wax or amorphous sulfur.

To operate the device it was assembled as shown. The plug (C) was removed and suction applied to form a moderate vacuum, The valve (E) **was** then closed tightly and the suction line was disconnected, leaving a vacuum in chamber (B). Dry air was blown through the chamber **(A).** The salt was next introduced into **(A),** and the solubility device was sealed onto the hydrogen fluoride delivery tube and the plug (C) was immediately inserted. This bore a gasket of wax or, at the higher temperatures, of 24 carat gold.

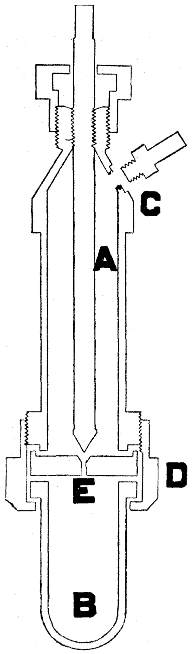

Fig. 1.—"Bomb," or solubility device.

The bomb was immediately placed in a constant temperature bath and shaken for two hours.

When time had been allowed for equilibrium to become established, the bomb was gently shaken in such a manner as to wash all the undissolved salt down into the corner of chamber **(A)** between the side and the bottom. The valve (N) was slowly opened two complete revolutions, then closed. The bomb was now removed from the thermostat. The plug (C) was removed, and the chamber **(A)** was washed out with concentrated hydrochloric acid followed by water, then dried by alcohol, ether and compressed air. The bomb and contents were now weighed on a large balance. The contents of B were washed into a platinum dish and evaporated. The bomb, platinum dish and contents were weighed. From these values the weight of the hydrogen fluoride and of the salt dissolved could be obtained by difference.

The bomb was made of monel metal. The absence of action on this material was shown by the failure to obtain tests for copper or nickel.

Potassium Iodide.—The salt was Mallinckrodt's "c. p." grade. It was screened with wire gauze to yield crystals between 12 and 20 mesh.

On treatment with liquid hydrogen fluoride in an open platinum crucible the solid apparently dissolved. However, when the solution was evaporated and the residue dissolved in water it was found that complete solvolysis had taken place. Only a slight turbidity resulted on treatment with silver nitrate, while a heavy precipitate followed the addition of calcium chloride solution to another portion of the solution. These tests indicate the absence of iodides and the presence of a fluoride. Gore[3] states that this salt is soluble but the present work shows that a reaction has taken place.

Chromium Fluoride.—The salt used was J. T. Baker Co.'s "C. P." grade. Concordant results could not be obtained with this salt even after weeks of experimentation, for unknown reasons. The material is plainly soluble.

Lithium Fluoride.—This salt was found to be quite soluble in liquid hydrogen fluoride. It reacts with the hydrogen fluoride as shown by the equation

$$\mathrm{LiF} + \mathrm{HF} = \mathrm{LiHF_2}$$

This is a good analogy to the reaction of lithium oxide with water

$$Li_2O + H_2O = 2LiOH$$

Not only so, but the solubilities of the two compounds in the respective solvents are of the same order.

Solubility data for the salt lithium fluoride are given for several temperatures in Table I.

TABLE I

SOLUBILITY DATA FOR LITHIUM FLUORIDE

Temp., °C.	Weight of HF	Wt. of Li_2SO_4	$\frac{\text{Moles LiF}}{\text{Moles HF}}$
0	12.347	1.421	0.043
0	4.229	0.4838	.043
10	7.510	.6661	.033
10	10.341	1.144	.041
20	5.214	0 6069	.044
30	4 399	.5386	.046
30	4.908	.5520	.042
30	7.138	.8084	.042
40	5.913	.7386	.046
40	10.460	1.215	.043

Calcium Fluoride.—Native fluorspar was screened to yield crystals of about 1 mm. diameter. These were then carefully hand picked, washed with hydrofluoric acid and dried, and cloudy crystals were rejected. No action occurred after four hours. The solubility was less than 0.01% at 0°.

Zinc Fluoride.—The salt was of the stock previously prepared in this Laboratory by the action of hydrofluoric acid upon pure zinc carbonate; solubility: less than 0.01% from —20 to +25°.

Magnesium Fluoride.—Magnesium fluoride was prepared by the method of C. Poulenc,[6] and that of F. Roder reported by Mellor.[7] Five grams of magnesium chloride and four grams each of sodium chloride and sodium fluoride were fused in a crucible and then cooled slowly. The resulting crystals were digested with water and well washed; solubility: less than 0.01% at 0°.

Discussion

A critical study of previous work on the physical and chemical properties of anhydrous liquid hydrogen fluoride suggests that the material is highly polar, and therefore should prove to be a good solvent for polar salts. The present work shows that for the fluorides of several elements of the first two groups of the periodic table the liquid is quite comparable to water.

It is desired to point out very clearly, however. that comparisons are to be made only between corresponding compounds. Thus lithium fluoride although insoluble in water is soluble in hydrogen fluoride. This compares to the solubility of lithium oxide in water. When solubilities are thus compared, considerable correspondence between the two solvents can be traced for the salts tested. When so compared, however, the solubilities in

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[6] C. Poulenc, *Ann. chim. phys.*, [7] 2, 5 (1894).

[7] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, p. 296.

hydrogen fluoride appear to be somewhat less than corresponding salts in water. Thus calcium and magnesium fluorides are less soluble in hydrogen fluoride than are the oxides in water, etc. Chromium fluoride seems to be an exception to this conclusion.

Summary

1. The solubility of lithium hydrogen fluoride between 0 and 40° has been established, and zinc fluoride, magnesium fluoride and calcium fluoride have been shown to be very insoluble. Potassium iodide has been found to react with liquid hydrogen fluoride. Chromium fluoride was found quite soluble but to an undetermined extent. These solubilities refer to liquid hydrogen fluoride as a solvent.

2. Comparison of these results indicates a fair similarity in the solvent action of water and hydrogen fluoride for the salts tried.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE STATE UNIVERSITY OF IOWA]

A METHOD FOR THE DETERMINATION OF CRITICAL TEMPERATURES AND THE CRITICAL TEMPERATURE OF HYDROGEN FLUORIDE

BY P. A. BOND AND DELLA A. WILLIAMS

RECEIVED JULY 28, 1930 PUBLISHED JANUARY 12, 1931

Accurate determination of the critical temperature by the usual method is difficult for several reasons. In the first place, glass is a poor conductor of heat and slight differences in bath temperature are not readily transmitted to the substance through the necessarily thick walls. Also for the same reason one end of the tube may be of slightly different temperature than the other. The gas above the critical temperature is very dense, diffusion is relatively slow and equalization of conditions in the tube does not readily take place. Some substances such as hydrogen fluoride attack glass and some such as nitrogen peroxide are so intensely colored at the critical temperature that observation is exceedingly difficult. The liability of tubes exploding under high pressures has also been a real difficulty where greater pressures are encountered. The method noted below permits the determination to be made without danger to the operator and under conditions of greater accuracy than those obtainable when the glass tube is used. Monel metal was used in the determinations because of its resistance to the action of hydrofluoric acid. Other metals could be used in the construction if desired.

Description of Apparatus

The critical temperature apparatus was composed of a constant temperature oven (Z), an assay balance (Y) and a critical temperature tube (D) (see Fig. 1). The critical temperature oven (Z) had an insulation of asbestos between the inner transite compartment (X) and the outer wooden box. The cover to the box was similarly insulated with asbestos. The heat was supplied by a resistance coil of nichrome wire (H). Circulation of the air inside was obtained by the use of the fan (A_1) propelled by the motor (A), the speed of which was regulated by a bank of lamps. After the oven had been heated for four hours and the heat and fan then turned off, a drop of but half a degree per minute was recorded. The readings were obtained from the thermometers E and E_1; one was placed in the corner of the oven and the other directly above the critical temperature tube.

The balance (Y) had the pan rests taken off, and a hole drilled through the base. At one end of the balance beam a platinum wire (F), size 50, was attached. The wire extended to the tube (D) and was of such length that the tube rested at an angle of about 20 degrees to the horizontal.

The critical temperature tube (see Fig. *2)* was 153 mm. long, 10 mm. diameter, with a wall 1 mm. in thickness. It was supported on steel knife edges (S) which rested on the polished surface of the support (C). The pointer (R), carrying the slide (V), was used to regulate the sensitiveness of the balanced system. A gold washer (U) was used to prevent leakage around the screw (T).

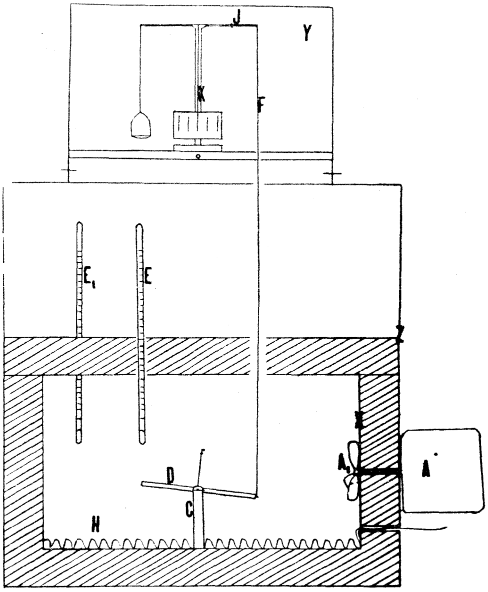
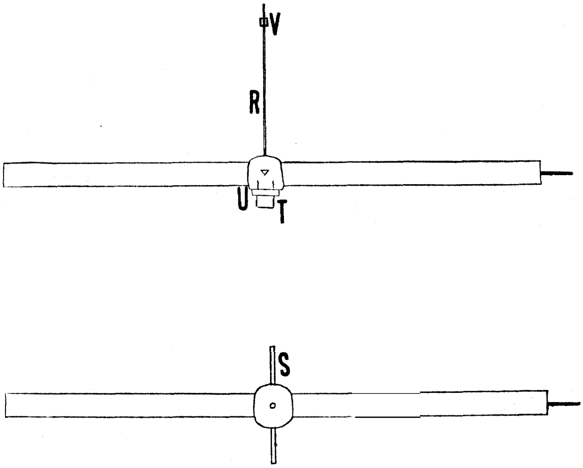


Fig. 1.

Manipulation

The critical temperature tube had a capacity of 1.88 cc. To insure that the tube was approximately half full of liquid, it was weighed after each filling. In order to be certain that there were no small leaks, the tube was allowed to stand for twelve hours and reweighed. If a constant weight was obtained, the tube was placed in the constant temperature oven. The oven had been heated previously, with the fan running, from three to four hours. The platinum wire was attached to the end of the tube and the oven again heated to above the critical temperature for more than an hour to insure constant temperature and uniform density of the gas within the tube. Differences in densities have been found to exist in the case of pure substances, above the temperature at which the meniscus disappears. According to Hein[1] in the case of pure carbon dioxide at 0.46' above the critical temperature seventy minutes elapsed after the disappearance of the meniscus before an equalization in density resulted.

When the thermometer read about 300° the fan and heat were both turned off. The system was balanced with the rider (J). When cooling had occurred to the critical temperature, the formation of the liquid phase in the lower end of the tube set the pointer of the balance in motion. The critical temperature was read at the first movement of the pointer.



Pig. 2.

The apparatus was checked using sulfur dioxide prepared according to the method employed by Stephens[2] and others in this Laboratory. The hydrofluoric acid was prepared by the method of Stowe.[3]

Results

The critical temperature of sulfur dioxide was found to be 157.8". This temperature checked in two tubes of the anhydrous liquid. Critical temperatures of sulfur dioxide determined previously were

155.4	Sajatschervsky[4]	157.15	Cardoso Bell[4]
156	Cailletet, Mathias[4]	157.8	Niggli[4]
157.263	Centnerszwer[4]	157	Drion[5]
157.20	Briner[4]	159	Sandenburg[5]
157.3	Travers[4]		

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[1] Hein, *Z. physik. Chem.*, **86**, 385–426 (1914).

[2] Bond and Stephens, THIS JOURNAL, 51, 2910 (1929).

[3] Bond and Stowe, *ibid.*, 53, 30 (1931).

[4] "Phys. Chem. Tabellen," 1923, p. 261.

[5] "Physico-Chem. Tables," 1911, Vol. I, p. 544.

The critical temperature of hydrogen fluoride was determined by this method. The tube was filled with fresh samples of the anhydrous liquid three times, and the following results were obtained

	Reading 1	Reading 2
First filling	230.2°	230.2°
Second filling	230.2	230.2
Third filling	230.0	....

Van Laar calculated the critical temperature of hydrogen fluoride using the formula[6]

$$\frac{T_c}{T_b} = K$$

Using $K = 1.7$, which is the average value of K as calculated from experimental values for hydrogen chloride, hydrogen bromide and hydrogen iodide

$$T_b = 292.5\text{°A.} = 19.5\text{°C.}$$

Substituting in $T_c = KT_b$

$$T_c = 497\text{°A.} = 224\text{°C.}$$

Substituting the observed critical temperature of hydrogen fluoride in the formula

$$\frac{T_c}{T_b} = K$$

we get the-value K = **1.72**, which is close to the observed values for hydrogen chloride, hydrogen bromide and hydrogen iodide.

Summary

A new method for the determination of the critical temperature has been developed. It may be used for substances which attack glass, and for those like nitrogen dioxide, where a meniscus cannot be observed. The critical temperature of anhydrous hydrogen fluoride was found to be **230.2°**.

The value of K in the formula $T_c/T_b = K = 1.72$ for hydrogen fluoride is very close to the average value as calculated from the observed boiling points, and critical temperatures of hydrogen chloride, hydrogen bromide and hydrogen iodide.

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[6] Van Laar, *J. chim. phys.*, **18, 273–282 (1920).**

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

REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION. I. INTRODUCTION

BY WILLIAM C. BRAY AND HERMAN A. LIEBHAFSKY

RECEIVED JULY 28, 1930 PUBLISHED JANUARY 12, 1931

Experimental data on the reactions that occur in acid solutions containing hydrogen peroxide, iodine and iodate ion will be presented in a series of papers. The rates of the following reactions have been measured: the oxidation of iodine to iodate

$$I_2 + 5\,H_2O_2 = 2\,H^+ + 2\,IO_3^- + 4\,H_2O \qquad (1)$$

the reduction of iodate to iodine

$$2\,IO_3^- + 2\,H^+ + 5\,H_2O_2 = I_2 + 6\,H_2O + 5\,O_2 \qquad (2)$$

and the catalytic decomposition of hydrogen peroxide

$$H_2O_2 = H_2O + {}^1/_2\,O_2 \qquad (3)$$

Our investigation was undertaken[1] with the hope of finding an intimate relationship between this catalysis and Reactions 1 and 2, in which the peroxide acts, respectively, as an oxidizing agent and as a reducing agent.

Reactions 1 and 2 were demonstrated by Auger[2] in 1911, and, independently, by Caulkins[1] in 1916–1917, but no evidence was presented that they could be obtained free, or nearly free, from the catalysis reactions. Recent experiments, however, have shown that under favorable conditions the amount of hydrogen peroxide catalytically decomposed is not over 5% of that used in Reaction 1, or 40% of that used in Reaction 2, though it may be much greater under other conditions.

We shall first consider the experimental conditions for realizing these reactions and also the well-known reactions of hydrogen peroxide with iodide and iodine

$$2\,I^- + 2\,H^+ + H_2O_2 = I_2 + 2\,H_2O \qquad (4)$$
$$I_2 + H_2O_2 = 2\,I^- + 2\,H^+ + O_2 \qquad (5)$$

The results of a number of qualitative experiments at room temperature are summarized in Table I; observations on catalytic decomposition of the peroxide and on tri-iodide formation are omitted to avoid confusion.

The complete transformation of iodide into iodine, Reaction 4, is possible at a sufficiently high concentration of hydrogen ion, as in Expt. *c;* the transformation of iodine into iodide, Reaction 5, may be accomplished without iodate formation by adding iodine (or tri-iodide) to an alkaline peroxide solution as in d. Both reactions may be demonstrated at a low concentration of hydrogen ion, as in Expts. b and *e;* in each case a steady

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[1] Bray and Caulkins, THIS JOURNAL, 43, 1262–1267 (1921).

[2] Auger, (a) Compt. rend., 152, 712–713 (1911); (b) *ibid.*, 153, 1005–1007 (1911); (c) in 1905 Skrabal, *Chem.-Ztg.*, 29, 554 (1905), reported iodate formation in acid solution as a result of the oxidizing action of hydrogen peroxide.

state is reached, which varies with the concentration of H^+, I^- and I_2, and in which Reaction **3** is the main or net reaction. This specific result was pointed out and studied quantitatively by Abel in 1908; his brilliant investigation have demonstrated that in this case the catalysis is completely accounted for by Reactions 4 and 5.

TABLE I

REACTIONS OF HYDROGEN PEROXIDE AT VARIOUS CONCENTRATIONS OF HYDROGEN ION

	Reaction of H_2O_2 with			
	I^-	I_2	$I_2 + IO_3^-$	IO_3
10^{-13} M $\overset{+}{H}$	a-—	*d* $I_2 \longrightarrow I^-$ very rapid	*g* $I_2 \longrightarrow I^-$ very rapid	*j* — –
10^{-5} M $\overset{+}{H}$	*b* $I^- \longrightarrow I_2$ moderate rate	*e* $I_2 \longrightarrow I^-$ moderate rate	h—	k $IO_3^- \longrightarrow I_2$ and I– very slow
1 0 M $\overset{+}{H}$	*c* $I^- \longrightarrow I_2$ faster than *e*	f ——	*i* $I_2 \longrightarrow IO_3^-$ rapid	*m* $IO_3^- \longrightarrow I_2$ faster than k

At moderate concentrations of iodate and acid, as in Expts. *i* and *m*, another similar steady state is reached, which varies with the concentrations of hydrogen ion, iodate ion, iodine and hydrogen peroxide. In *i* the transformation of iodine into iodate, Reaction 1, takes place rapidly; while in *m* the much slower complementary reaction, 2, can be demonstrated easily only by removing the iodine as it is formed, *e.* g., by extraction with carbon tetrachloride. In the latter case, if the iodine is not removed, the observed reaction is a slow catalytic decomposition of the peroxide. The demonstration of Reaction 2 is more easily accomplished at a somewhat lower concentration of hydrogen ion, since the steady state concentration of iodine is then larger. In alkaline solutions, however, as in Expt. **j**, the amount of iodate reduced (to iodide) is practically zero;[4] the relatively rapid decomposition of the peroxide, $HO_2^- = OH^- + {}^1/_2 O_2$, prevents the detection of the extremely slow reduction of the iodate.

Both iodate and acid are necessary for the immediate and rapid oxidation of iodine to iodate, Expt. *i*. Thus in the absence of iodate, as in Expt. f, iodine in solution with hydrogen peroxide and acid remains apparently unchanged for several hours before being oxidized. Small initial concentrations of iodate shorten the induction period; but Reaction **1**, when once

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[3] Abel, (a) *Z.* Elektrochem., 14, 598–607 (1908); (b) Monatsh., **41,** 405–421 (1920); (c) *Z. physik. Chem.*, 96, 1–179 (1920); (d) *ibid.*, **136,** 161–182 (1928).

[4] This is in agreement with the results of Skrabal, Monatsh., 32, 868 (1911), and of Tanatar, Ber., **32,** 1013 (1899); **33,** 205 (1900). At sufficiently low concentrations of hydroxide ion some reduction to iodide is easily demonstrated. Thus in experiments by Caulkins at 60°, in which the initial concentrations were 0.094 M KIO_3, 0.193 M H_2O_2 and (a) 0.022 M NaOH, (β) 0.0026 M NaOH, and the colorless solutions were acidified after nearly all the peroxide had decomposed, appreciable amounts of iodine were formed in (β), but not in(or). By assuming the ionization constant $(H^+)(HO_2^-)/(H_2O_2) = 2.5 \times 10^{-12}$, the initial OH^- concentration is found to be approximately 3×10^{-4} M in (a) and 3×10^{-5} M in (β).

started, proceeds at a rate that is not greatly influenced by changes in the concentrations of iodate, acid and peroxide. Similarly, on lowering the acid concentration in the presence of iodate, induction periods are again encountered; these increase in length until finally Reaction 1 does not take place in the neighborhood of the hydrogen-ion concentration of Expt. *h*.[5] Reaction 1 is thus seen to be autocatalytic only in the sense that the products, iodate and hydrogen ions, eliminate the induction period.

On account of the speed with which iodide, iodate and hydrogen ions react when all are present at rather low concentrations, it is evident from the above results that Reaction 1 takes place only when the iodide concentration does not exceed an extremely small value. Iodide, when present, as in the work of Abel,[3] would react with, or prevent the formation of, intermediate products which are necessary in the oxidation of iodine by hydrogen peroxide. This explanation may not suffice when the solution is alkaline or the concentration of hydrogen ion is very small, but in these cases intermediate products, as hypoiodite, are reduced very rapidly to iodide ion by the peroxide (cf. Expts. g and *d* in Table I). It is thus not surprising that Abel[6] found no trace of iodate in any of his experiments with Reactions 4 and 5 and the related catalysis.

The elimination of the induction period in Reaction 1 involves a transition from the iodide to the iodate regions, *e*. g., from *b* e to *i* m in Table I. The periodic reaction,[1] announced in 1921 as the first example of periodicity in homogeneous solutions, also lies in this transition region, and illustrates its complexity. Rice and Reiff[7] have questioned this claim of homogeneity, and ascribe the periodicity to the presence of minute dust particles. As we have not repeated the experiments of Rice and Reiff, and our own investigation of the periodicity is by no means complete, we have nothing definite to contribute on this question. We must state, however, that in 1922 Bon repeated and extended Caulkins' measurements on periodic oxygen evolution at 60°. Also in our recent work Liebhafsky has made some incidental observations on periodicity in oxygen evolution at 50° and in iodine formation at 0°. On account of the regularity of the results, and their occurrence in the transition region referred to above, we still believe it possible that the periodicity depends on a system of homogeneous reactions, at least one of which is autocatalytic.

While Brode[8] seems to have been the first to state clearly the role of hypoiodite as an intermediate step both in the catalytic decomposition of hydrogen peroxide in an initially neutral iodide solution and in Reaction

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[5] An effect of the addition of acid similar to that in the series d e f, and the final transition to iodate formation, were noted by Skrabal in 1905; Ref. 2 c.

[6] Abel, Ref. 3 c, p. 30.

[7] Rice and Reiff, *J. Phys. Chem.*, 31, 1352 (1927).

[8] (a) Brode, *Z. physik. Chem.*, 49, 208 (1904); (*b*) cf. Bray, *ibid.*, 54, 485 (1906).

4, we owe to Abel[3] the complete demonstration of the mechanism of the iodide–iodine reactions with hydrogen peroxide. His conclusions and those of Bray and Livingston,[9] in the case of the analogous bromide–bromine–peroxide reactions, are in close agreement, and thus support each other. In fact, these investigations furnish two examples in which the proof of mechanism may be regarded as satisfactory. For the mathematical treatment of the results the reader is referred to the original articles, particularly References 9a, 9*c* and 3d.

All bromide–bromine reactions with hydrogen peroxide in dilute acid solutions depend upon only two rate-determining steps

$$X^- + H^+ + H_2O_2 \longrightarrow HXO + H_2O \qquad (6a)$$
$$HXO + H_2O_2 \longrightarrow X^- + H^+ + H_2O + O_2 \qquad (6b)$$

and the relatively rapid reversible reaction

$$X_2 + H_2O \rightleftharpoons HXO + H^+ + X^- \qquad (6c)$$

Corrections in the concentrations of bromide ion and bromine due to

$$X_2 + X^- \rightleftharpoons X_3^- \qquad (6d)$$

are in general small. The ionization of hypobromous acid can be neglected except in alkaline solutions

$$HXO \rightleftharpoons H^+ + XO^- \qquad (6e)$$

In the case of pure catalysis the absolute rates of the two compensating reactions, 6*a* and 6*b*, are equal at any instant; but the specific reaction rate of the third order reaction, 6*a*, is extremely small in comparison with that of the second order reaction, 6*b*, with the result that the steady state concentration of HXO is always extremely small compared with that of X^-.

In the iodide–iodine reaction 6*a* and 6*b* are each accompanied by a second reaction

$$X^- + H_2O_2 \longrightarrow XO^- + H_2O \qquad (6a')$$
$$XO^- + H_2O_2 \longrightarrow X^- + H_2O + O_2 \qquad (6b')$$

At low concentrations of hydrogen ion Reaction 6*a* can be neglected in comparison with 6*a'*, but both 6*b* and 6*b'*, and therefore the equilibrium 6*e*, must be considered. The concentration of tri-iodide ion is in general much greater than that of iodine, 6*d*. Finally, and this is the most serious difficulty, the hydrolysis equilibrium, 6c, is not established sufficiently rapidly to prevent the direct and reverse reactions from appearing as rate-determining steps in many of the experiments.[3d]

The mechanism of the iodine–iodate–hydrogen peroxide reactions undoubtedly involves intermediate substances, such as I^-, HIO and HIO_2, which are present at very small concentrations. The number of such compounds that may be postulated is very great, and any discussion of inter-

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[9] (a) Bray and Livingston, This Journal, 45, 1251 (1923); (b) 2048 (1923); (c) 50, 1654 (1928); (d) Livingston, *ibid.*, 48, 53 (1926).

mediate reactions which is qualitative in character or based on incomplete data must be regarded as tentative. The present introduction, accordingly, is intended merely to pave the way for the discussion of mechanism in later papers.

The simplest direct line between iodide and periodate in acid solution is represented by the series

$$I^-, HIO, HIO_2, IO_3^-, IO_4^- \qquad (7)$$

Hypoiodous acid is an extremely weak acid.[10] Iodous acid, which has not been isolated, is to be regarded as a fairly weak acid by analogy with chlorous and nitrous acids, and the remaining three acids are relatively strong electrolytes. While it is practically certain, on the basis of free energy considerations[1,9a] alone, that hydrogen peroxide is capable of oxidizing each substance in the list (except IO_4^-) and of reducing each (except I^-) in reactions similar to 6*a* and 6*b*, the speed of several of these reactions must be concluded to be negligibly small on account of either known stoichiometric results, or the effect of other oxidation–reduction reactions.

Thus Reaction 5 has been isolated by Abel,[3c] free from catalysis, Reaction 3; it follows that under his experimental conditions the rate of the reaction

$$HIO + H_2O_2 \longrightarrow HIO_2 + H_2O \qquad (8)$$

is negligible in comparison with that of

$$HIO + H_2O_2 \longrightarrow H^+ + I^- + H_2O + O_2 \qquad (9)$$

since any HIO_2 formed in 8 would be reduced by H_2O_2 or by $I^- + H^+$, thus giving catalytic decomposition as the net result. We shall assume that Reaction 8 remains negligible in comparison with 9 at the higher acid concentration of our experiments, and at all concentrations of HIO and H_2O_2. Similarly we may conclude, from our evidence as to the isolation of Reaction 2, that the reaction

$$IO_3^- + H_2O_2 \longrightarrow IO_2^- + H_2O + O_2, \text{ or} \qquad (10a)$$

$$IO_3^- + H^+ + H_2O_2 \longrightarrow HIO_2 + H_2O + O_2 \qquad (10b)$$

is more rapid than

$$IO_3^- + H_2O_2 \longrightarrow IO_4^- + H_2O \qquad (11)$$

If the formation of periodate were the only primary step in this reaction, *as* suggested by Tanatar[4] to account for the catalytic action of iodic acid, then the amount of peroxide decomposed catalytically would be at least 80% in excess of that required by Equation 2, which is much greater than the lowest figures in our experiments. The assumption that HIO_2 and IO_2^- are the primary products in the reduction of IO_3^- by H_2O_2 is in agreement with our rate measurements; and we have, somewhat arbitrarily it is true, omitted IO_4^- from further consideration.

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[10] Fürth, *Z. Elektrochem.*, 28, 57 (1922), gives 10^{-11} as an approximate value for its ionization content **at** 25°.

The possibility of the oxidation of iodide ion by hydrogen peroxide, Reactions 6a and 6a′, must be rejected on account of the presence of acid and iodate. Under these conditions, as has already been indicated in this paper, iodide is oxidized much more rapidly by iodate[11] than by hydrogen peroxide.[12] However, this rapid iodate–iodide reaction is probably also relegated to the background (except in induction periods) by the reaction between iodous acid, I^- and H^+, which must have an extremely high specific rate.

Accepting the convention that second and third order reactions are more probable than those of higher orders, we shall write this reaction in two steps

$$HIO_2 + I^- + H^+ \longrightarrow 2\,HIO + H_2O \qquad (12)$$

$$HIO + I^- + H^+ \rightleftharpoons I_2 + H_2O \qquad (13)$$

The equilibrium in 13 (*cf.* 6*c*) is assumed to be maintained except in the very rapid oxidation of iodine to iodate, Reaction 1.

The reduction of HIO_2 by H_2O_2 is also conceivable

$$HIO_2 + H_2O_2 \longrightarrow HIO + H_2O + O_2 \qquad (14)$$

but this reaction cannot be considered apart from the oxidation of HIO_2 by H_2O_2

$$HIO_2 + H_2O_2 \longrightarrow IO_3^- + H^+ + H_2O \qquad (15)$$

The latter seems to be a necessary step in the very rapid oxidation of I_2 to IO_3^-, Reaction 1, in the presence of moderate concentrations of H^+ and IO_3^- (*cf.* *i* in Table I). Our evidence on the isolation of Reaction 1, nearly free from catalysis, leads to the conclusion that under these conditions the specific rate of Reaction 15 is very great in comparison with that of 14.

The hydrogen peroxide reactions in acid solution that have not been eliminated by the foregoing conclusions are Nos. 9 and 10 in which the peroxide acts as a reducing agent, and No. 15 in which it acts as an oxidizing agent.

The series of intermediate reactions, 10–12–9–13, is in substantial agreement with our rate data for Reaction 2; Nos. 10 and 15 account partly, but far from completely, for the catalysis, and the following steps are available to explain Reaction 1: the hydrolysis of iodine (the reverse of No. 13), the oxidation of iodide presumably to hypoiodous acid by iodate[11] and by iodous acid (No. 12), and the oxidation of iodous acid by hydrogen peroxide (No. 15). It will be noted that in the last series an additional assumption is necessary to account for the rapid oxidation of iodine above the hypoiodite state. Several possibilities are being con-

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[11] (a) Abel and Stadler, *Z. physik. Chem.*, 122, 49 (1926); (b) Abel and Hilferding, *ibid.*, 136, 186 (1928); (c) Dushman, *J. Phys. Chem.*, 8, 453 (1904); (d) Skrabal, *Z. Elektrochem.*, *28*, 224 (1922); **30**, 109 (1924).

[12] (a) Harcourt and Esson, *Phil.* Trans., 157, 117 (1867); (b) Noyes and Scott, Z. *physik. Chem.*, 18, 118 *(1895);* (c) *cf.* Bray, *ibid.*, 54, 486 (1906).

sidered and will be discussed in later papers. At the present time the favored explanation involves the intermediate substance, $H_2I_2O_3$ or I_2O_2, discussed by Bray in a recent paper.[13]

Summary

The experimental conditions under which the various reactions of hydrogen peroxide in acid solutions containing iodine and iodate or iodide take place have been discussed, and the mechanism of these reactions briefly considered.

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

REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION.

II. THE PREPARATION OF IODIC ACID. PRELIMINARY RATE MEASUREMENTS

BY WILLIAM C. BRAY AND A. L. CAULKINS

RECEIVED JULY 28, 1930 PUBLISHED JANUARY 12, 1931

On the basis of our first experiments on the oxidation of iodine to iodic acid by hydrogen peroxide (Reaction 1, Part I),[1] a method of preparing iodic acid and iodine pentoxide on a small scale was outlined for use in an undergraduate course. While this method is not as satisfactory as the more recently developed one in which a concentrated solution of chloric acid is the oxidizing agent,[2] its description affords a convenient way of presenting a number of experimental results.

Materials.—Ten grams of very finely divided iodine (resublimed, crystalline iodine is far less satisfactory than that recovered from an iodide solution by precipitation with an oxidizing agent, as chlorine, or hydrogen peroxide at high acid concentration); 10 cc. of concentrated nitric acid; 300–400 cc. of 3% hydrogen peroxide, which is 1.5 to 2 times the theoretical amount required.

Directions.—Place the iodine, nitric acid and about 50 cc. of the peroxide solution in a 750-cc. flask and heat the mixture in a water-bath at about 70°. To minimize the loss of iodine vapor, place a loosely-fitting glass stopper or small funnel in the mouth of the flask. Shake the flask frequently when the solution does not show a deep color due to dissolved iodine. Observe when the reaction starts, as shown by the first decrease in color. Whenever the solution again becomes deeply colored, add more hydrogen peroxide. Continue until the solid iodine (or the hydrogen peroxide) is consumed. Evaporate the solution rapidly to a small volume.

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[13] Bray, THIS JOURNAL, 52, 3580 (1930).

[1] Part I. Bray and Liebhafsky, THIS JOURNAL, 53, 38 (1931).

[2] Lamb, Bray and Geldard, *ibid.*, 42, 1636 (1920).

To remove the nitric acid and the organic substances introduced with the peroxide, evaporate the solution to dryness in a small porcelain dish; heat the residue in a drying oven for at least two hours, at first at 140–150° and later at 170–180°; extract the iodic acid with boiling water, filter off and reject the dark-colored residue. Evaporate the solution to dryness, and partially dehydrate the solid by heating it in a drying oven at 150–200°, carefully avoiding overheating.

If the product is still dark-colored, add some concentrated nitric acid and treat the mixture again as described in the preceding paragraph, or proceed as follows.

To prepare crystalline iodic acid, HIO_3, dissolve nearly all of the partially dehydrated solid in the minimum amount of hot water, filter, cool the filtrate, place the clear solution in a crystallizing dish in a vacuum desiccator over anhydrous calcium chloride and seed with a crystal of iodic acid if this is necessary. Finally, reject the mother liquor when only a small portion remains, and wash the crystals with a few drops of cold water.

Notes.—While in 0.1 N acid at 25° the reaction between iodine and hydrogen peroxide will not start for several hours, it starts rapidly at a temperature of 70–80° when the acid concentration is molal or greater. When once started the reaction in the solution is rapid even at a low temperature, and the limiting factor is the rate of solution of the solid iodine. For this reason the high temperature is maintained, finely divided iodine is used, and the mixture is shaken frequently. Since hydrogen peroxide reacts also with iodic acid (*cf.* Expt. m, Part I), catalytic decomposition is unavoidable; a 50% excess of peroxide is required in the procedure as here outlined, but much more may be used if the shaking is neglected.

The process would be much more satisfactory if hydrogen peroxide were available at higher concentration and free from preservative. The organic material is partially decomposed and rendered insoluble in the evaporation and subsequent heating, presumably on account of the presence of the nitric acid; but the product is not as white as that obtained with chloric acid.[2]

The yield with respect to iodine is practically quantitative. There is danger of loss by decomposition during the heating of the solid product only if the temperature is not properly controlled, but the permissible temperatures are lower than for material prepared by the chloric acid method,[3] and our product is thus less completely dehydrated.

The Rate of Oxidation in Homogeneous Solution.—In agreement with the observation, noted above, that the reaction proceeds rapidly when once started, it was found that the reaction also starts rapidly when iodate and acid are present initially. The kinetic investigation of this reaction in homogeneous solution was then undertaken. Nearly all the measurements were made at 25°.

[3] *Cf.* Ref. 2, pp. 1644-1645.

A large quantity of a nearly saturated solution of iodine in conductivity water was kept in a thermostat in contact with finely divided iodine, and portions were withdrawn through an asbestos filter. Standardized stock solutions of potassium iodate, sulfuric acid and hydrogen peroxide were also suspended in the thermostat. In each experiment known amounts of iodate and acid were added to a known volume of the iodine solution, the mixture was shaken, after ten minutes a measured volume of the peroxide solution was added rapidly and the mixture was again shaken. The rate was followed by determining the concentration of iodine in samples pipetted out of the reaction mixture. On account of the high speed of the reaction the first samples were withdrawn as rapidly as possible. The first order rate constant was calculated for successive pairs of results by means of the formula

$$k = \frac{2.3}{t_{n+1} - t_n} \log \frac{(I_2)_n}{(I_2)_{n+1}} \tag{1}$$

The units are moles per liter and minutes. The time at which half the peroxide had been added was recorded as t_0. The initial concentration of iodine, $(I_2)_0$, was calculated from the concentration of the stock solution and the volumes of the various solutions taken. A reasonable check was furnished by the analysis of the first sample in a few cases in which there was a noticeable induction period.

The reaction was stopped by adding each sample withdrawn for analysis to carbon tetrachloride and shaking the mixture at once. The time of shaking was recorded as t_n. The corresponding concentration of iodine, $(I_2)_n$, was determined by carefully separating the phases as soon as was convenient, adding the carbon tetrachloride layer to a solution of potassium iodide, and titrating with thiosulfate. Sources of error and further experimental details will be discussed in a later paper. At the present time it is sufficient to note that fairly definite results were obtained by increasing the number of identical or similar experiments.

Thirteen sets of experiments were performed at 25°, with enough duplicates to bring the total to twenty-eight. The range of concentrations covered was as follows

KIO_3, 0 0069–0 042 *M* (6-fold)
H_2SO_4, 0 015–0 300 N (20-fold)
H_2O_2, initial, 0 006–0 210 **(35-fold)**

Typical results are shown in Fig. 1. Values of k are plotted against the concentration of iodine, each concentration being the mean of the initial and final values used in calculating k. To show the high speed of the reaction, the successive time intervals in Expt. A are recorded, in minutes: 1.08, 0.58, 0.59, 0.67, 1.25, 1.02, 28.17. The half time is approximately one minute.

All the experiments were in accord with the following conclusions: the values of k are nearly constant at concentrations of iodine from 1 × to 3 × 10^{-4} *M* (and in some cases to 1.5 × 10^{-4} M), but always fall off markedly at lower concentrations; the "constant" is independent of the concentrations of iodate, acid and peroxide within the ranges investigated. The average, $k = 0.6 \pm 0.1$, was chosen at the time; but single values sometimes deviated from this by as much as ±0.3, and the possibility of a gradual decrease of k during a run was not excluded.

Four experiments at 0°, in which the concentrations of iodate and acid were close to 0.018 *M* and 0.12 *N* and that of the peroxide was varied between 0.033 and 0.093 M, gave an average value of k of 0.027 ± 0.002; but this should be neglected for the present, since the iodate and acid were not varied.

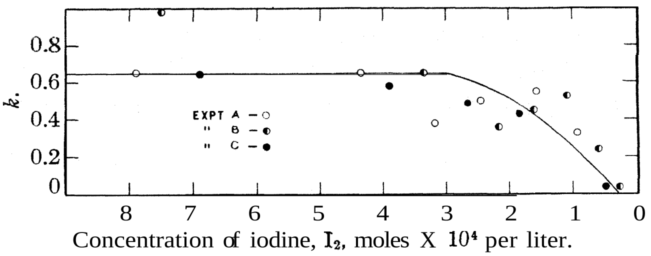

Fig. 1.—Values of the specific reaction rate in three experiments. Initial concentrations: in Expts. A and B, 0.010 M KIO_3, 0.130 *N* H_2SO_4, 0.106 M H_2O_2; in Expt. C, 0.031 *M* KIO_3, 0.130 N H_2SO_4, 0.042 M H_2O_2.

In 1920 similar measurements were made at 25° by Bray and Dr. Harry East Miller, to determine whether the earlier results could be checked, and whether traces of chloride ion played an important role in the reaction. The accelerating effect of chloride had been stressed by Auger (Ref. 2a, Part I). The only difference in procedure was that the iodine was dissolved in an iodic acid solution instead of in distilled water.

In several experiments with 0.043 *M* HIO_3 and 0.013 to 0.042 *M* H_2O_2, k was again found to be 0.6, and the variations were within ±0.1 or less, down to a concentration of iodine between 1 and 2 × 10^{-4} *M*.

In two experiments with higher peroxide concentration, 0.086 M and 0.045 M HIO_3, a decrease of k from 0.6 to about 0.4 was observed in the iodine range where constancy had been observed in other cases. Also, when the iodate concentration was decreased to 0.0090 *M*, lower values of k were obtained: approximately 0.3 with iodic acid alone, and 0.5 when enough sulfuric acid was added to make the acid concentration 0.045 *N*. The earlier statement as to the constancy of k must therefore be regarded as approximate rather than exact.

The effect of the presence of chloride is shown by the results of experiments with 0.045 *M* HIO_3 and 0.013 M H_2O_2, in which the initial concentrations of chloride due to added potassium chloride were 0.0, 0.268×10^{-4} and 1.34×10^{-4} M; the corresponding values of k were 0.6, 0.66 (constant), and 1.0 (decreasing to 0.8). It is evident that the amount of chloride impurity present in our solutions was too small to influence the results.

The simplest interpretation of our results is that the first order reaction is the rate of hydrolysis of iodine, and that the rapid decrease of k at low iodine concentration is due to the effect of the reverse reaction as the hydrolysis equilibrium is being approached. From a consideration of the equations

$$I_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} HIO + H^+ + I^- \tag{2}$$

$$-d(I_2)/dt = k(I_2) = k_1(I_2) - k_2(HIO)(H^+)(I^-) \tag{3}$$

it is evident that k, calculated from the experimental data by means of Equation 1, will be equal to k, when $k_2(HIO)(H^+)(I^-)$ is negligible in comparison with k_1 (I_2) provided that *(2)* is the only reaction in which iodine is being consumed.

The probability of a direct relation to the rate of iodine hydrolysis was recognized from the first; but we hesitated to publish this conclusion before additional evidence was available. This has now been supplied by the recent work of Abel, referred to in Part I (Ref. 3 d), on the reaction of iodine and iodide with hydrogen peroxide (in the absence of iodate); and our results in turn furnish a confirmation of the mechanism he proposes. By means of a mathematical analysis of these reactions, and his own experimental data at 25° for 0.4 M sodium acetate solutions, he concluded that $k_1 = 0.25$. Higher values 0.38–1.1 were obtained from less extensive data for more concentrated acetate solutions, but were considered less reliable. The agreement between our "constant," 0.6 and Abel's values of k_1, is very striking.

We have concluded that the oxidation of iodine by hydrogen peroxide furnishes a direct method of investigating the rate of hydrolysis of iodine, Equation 2.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY. UNIVERSITY OF WISCONSIN]

EFECT OF HYDROGEN-ION CONCENTRATION ON THE FLOCCULATION VALUES OF FERRIC OXIDE SOLS. I

BY FRED HAZEL AND C. H. SORUM

RECEIVED OCTOBER 2, 1930 PUBLISHED JANUARY 12, 1931

Preparatory to the investigation of an irregular series for colloidal iron oxide, using potassium ferrocyanide as the added electrolyte when working with sols of various H^+-ion concentrations, it has been thought worth while to observe the behavior of these sols with a representative list of ions which do not produce the recharging phenomena. It is well known that colloidal iron oxide when freshly prepared by hydrolysis of ferric chloride contains, as the chief contaminants, hydrochloric acid and ferric chloride in relatively large quantities. Moreover, such sols show great stability toward added electrolytes. However, much of this stability is lost when the colloid is dialyzed and the impurities subsequently removed.

In the following study a large volume of a stock sample of the sol was prepared by hydrolysis of ferric chloride and dialyzed for a week or more at a temperature ranging between 80 and 90°. Later measurements showed the product to be quite free from hydrochloric acid, the P_H of the purified system being above 6. To obtain sols with a suitable range of hydrogen-ion concentrations the stock sample was diluted thus

Sol number	Diluted with
1	Equal volume of water
2	Equal volume of approximately $N/5000$ HCl
3	Equal volume of approximately $N/2000$ HCl
4	Equal volume of approximately $N/1000$ HCl
5	Equal volume of approximately $N/500$ HCl
6	Equal volume of approximately $N/200$ HCl

Concentration of sol (before dilution), 1.24 g. Fe/ liter

The H^+-ion concentrations were determined with a glass electrode of the type described by MacInnes and Dole.[1] The membranes were from a glass recommended by them and were about 10 mm. in diameter. A vacuum tube potentiometer was selected for a "null" instrument. The apparatus is described by Partridge.[2] The circuit was modified, however, in that a wall galvanometer was used in place of the milliammeter and a student potentiometer in place of the voltmeter in his hook-up. The principle of operation is the same in both instances but the substitution of the galvanometer permits the use of a triode plate current which is much smaller (of the order of magnitude of 10^{-6} ampere) than that employed in the original device. P_H determinations on buffer solutions

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[1] MacInnes and Dole, THIS JOURNAL, 52, 29 *(1930).*

[2] Partridge, ibid., 51, 1 (1929).

made with this set-up using glass electrodes have been checked against values obtained with an ordinary, although accurate, hydrogen electrode circuit and have been found to agree within 0.03 of a *PH* unit. Hydrogen-ion concentrations of the sols in this study were checked numerous times with as many as eight different glass electrodes, the results deviating by not more than ±0.05 of a *PH* unit from the value given. (*PH* values have also been determined in other systems where repeated trials have given results dependable to 0.1 of a *PH* unit.[3] Among these systems may be mentioned Fe_2O_3 sol + H_2O_2; acid + H_2O_2; concentrated acid + $SnCl_2$; and methylene blue + hypochlorite.)

[3] Standardization of the electrodes was accomplished by measuring the potential against buffer solutions the *PH* of which had been previously determined by means of a hydrogen electrode. Thus if the e. m. f. of a cell

$$\begin{array}{c|c|c|c} \text{Ag--AgCl} & \text{Glass} & \text{Buffer} & \text{Satd. KCl} \\ 0.1\ N\ \text{HCl} & & P_H\ 4.0 & \text{calomel} \end{array}$$

is 0.135 v., the constant of the circuit, which compensates for any current flowing through the cell at balance and also includes the asymmetry potential of the glass membrane, may be calculated by the equation

$$P_H = \frac{E_{\text{cell}} + C}{0.059} \text{ at } 25^\circ$$

Substituting the values of *PH* and E, we have

$$4.0 = \frac{0.135 + C}{0.059} \text{ or } C = 0.101 \text{ v.}$$

Providing this particular electrode is sensitive to the right degree to changes in H+-ion concentration, it should show for a buffer of *PH* 5.0 an e. m. f. equal to that calculated from the preceding formula

$$5.0 = \frac{E + 0.101}{0.059} \text{ or } E = 0.194 \text{ v.}$$

Similarly a buffer of *PH* 6.0 should have an E value 0.059 v. higher than that for a solution of *PH* 5.0. Of course this is true only if the constant of the circuit has undergone no change during the measurements; hence it is of advantage to check the constant before and after each determination using the standard buffer of *PH* 4.0.

It has been found in the present work that newly prepared electrodes are rarely suitable for immediate use. Thus when a freshly blown electrode completes a cell containing a buffer of *PH* 4 0 it may show a potential of greater than 0.6 v. It is impossible to work with such an electrode because the initial value of E is not constant. The high value of E indicates a large membrane potential. Moreover, such electrodes in the circuit seem to introduce capacity effects that make conditions such that measurements are not practical with the potentiometer described. However, upon aging these electrodes in an acid solution of more or less indifferent concentration, the value of E decreases until after several days it becomes practically constant. In other words, equilibrium is established in the membrane and the asymmetry potential is constant in so far that the constant, C, of the circuit does not vary over ±0.005 v. during a day's run. Happily, also, capacity effects are absent at equilibrium and the electrode can be used for accurate measurements in a cell unprotected by shielding. It has also been found that when newly prepared electrodes show an initial value of E in the vicinity of zero, for the cell containing the standard buffer, they are sluggish in detecting changes in hydrogen-ion concentration even after weeks of aging.

Flocculation values were obtained by adding 2 cc. of sol to 3 cc. of electrolyte in 12.7-cm. pyrex test-tubes and permitting to stand for twenty-four hours. Those concentrations which were just sufficient to produce complete coagulation in the allotted time were taken as the limiting values, the so-called flocculation value being calculated in millimoles per liter from the latter in the usual manner. While this method has its recognized disadvantages, it was applicable in the present case where relative measurements were sought.

Table I includes representative data for some typical electrolytes. The *P*H was determined after two volumes of the particular sols, whose flocculation values are given, were diluted with three volumes of distilled water.

Table I

Representative Data

Sol	**1**	**2**	**3**	**4**	**6**	**6**
*P*H	**5.9**	**5.4**	**4.6**	**3.9**	**3.4**	**2.9**
		Flocculation values in millimoles/liter				
KCl	16	32	56	76	100	120
KBr	16	32	56	80	100	120
NH_4Cl	12	16	40	68	92	116
$^1/_2$ $BaCl_2$	24	40	88	144	208	
$^1/_3$ $FeCl_3$	252	252	252	252	252	252
$^1/_3$ $AlCl_3$	360	360	360	360	360	360
K_2SO_4	0.125	0.12	0.11	0.10	0.09	0.08
$(NH_4)_2SO_4$		.125	.115	.100	.090	.075
$CaSO_4$	.15	.15	.14	.12	.11	.10
K_2CrO_4	.05	.06	.08	.12	.16	.19
$K_2Cr_2O_7$	.030	.04	.065	.080	.090	.100
$K_3Fe(CN)_6$	.016	.020	.026	.026	.026	.026
KH_2PO_4	.036	.048	.064	.072	.088	.104
$K_4Fe(CN)_6$	.012	.016	.024	.028	.028	.028

The electrolytes in the table may be divided into groups: Group I, which includes uni-univalent salts; Group 2, represented by barium chloride; Group 3, represented by ferric chloride and aluminum chloride; Group 4, including potassium sulfate, ammonium sulfate and calcium sulfate; Group 5, with potassium chromate and potassium dichromate; Group 6, which contains potassium ferricyanide and primary potassium phosphate; finally, Group 7, with potassium ferrocyanide.

With a positive sol, such as those used in the present work, the anion of the added electrolyte is the effective agent in producing coagulation. Hence we observe that the flocculation values for the monovalent anions are relatively higher than those for the bivalent ions and these in turn are higher than those for trivalent anions. The reason for the above grouping of electrolytes will become apparent with this and the following considerations. It can be noted that in groups one and two the flocculation values of the sols increase strongly and regularly with increase in hydrogen-ion concentration of the sols. On the other hand ferric chloride and aluminum chloride do not show any variation in this property. of the colloid with changes in the initial *PH* of the sol. The anomaly in the behavior of these two salts is explained by examination of the data in Table II, which gives the *PH* of the sols after dilution of two volumes of the sol with three volumes of water. The *PH* of the coagulated medium obtained by adding the critical concentration of certain of the electrolytes is also shown.

TABLE II

EXPERIMENTAL DATA

Sol.	1	2	3	4	5	6
After dil.	5 9	5.4	4.6	3.9	3.4	2.9
KCl	6 9	5 4	4 7	4.0	3.4	
NH_4Cl	6 0	5 5	4 7	3 9	3.4	2.9
$FeCl_3$	1 7	1 7	1.7	1.7	1.6	1.7
$AlCl_3$	3.5	3 5	3 5	3.5	3.5	3.5
K_2SO_4	6.4	6 0	5 1	4.1	3 5	3.0
$(NH_4)_2SO_4$		6 3	5 5	4 2	3.5	3.0
$K_3Fe(CN)_6$	6 3	6 0	4 9	4.1	3.5	3.0

According to the data in this table, if the *PH* of the coagulated system is determined after the addition of the flocculating concentration of either ferric chloride or aluminum chloride, the *PH* values are constant regardless of the initial PH of the sol. Both aluminum chloride and ferric chloride, being salts of a strong acid and weak bases, hydrolyze to a pronounced degree when dissolved in water to give hydrochloric acid as one of the products. We may then consider that when we use these salts as the coagulators we are adding not only the ions of the salts but also hydrogen ions. The amount of the latter derived by the introduction of the salt in any case will depend, among other things, upon the concentration of hydrochloric acid already present. For example, an aluminum chloride solution of a given concentration when added to sol number 1 with a H^+-ion concentration corresponding to a *PH* of 5.9 will hydrolyze to a greater extent and hence produce more hydrochloric acid than in the case of sol number 6 where the *PH* is 2.9. *In* the simple case we may be dealing with the equilibria

$$AlCl_3 + H_2O \rightleftharpoons AlOHCl_2 + H^+ + Cl^-$$

or

$$2\ AlCl_3 + 6\ H_2O \rightleftharpoons 2\ Al(OH)_3 + 6\ H^+ + 6\ Cl^-$$

and

$$HCl \rightleftharpoons H^+ + Cl^-$$

so that a buffer action is maintained by the common ion effect and enables the one or the other reaction to be reversed, making the gross hydrogen-ion concentration constant.

Freundlich[4] states that small concentrations of hydroxyl ions raise the stability of negative sols but that the symmetrical effect of the H^+ ion with positive sols is less clearly visible since the latter are almost all hydroxide sols so that a chemical action takes place. (Incidentally, in the present work the concentration of acid used in charging the sols did not go above $N/200$ and the amount of ferric ion produced by the solvent action was only sufficient to give a very faint coloration with the ammonium sulfocyanate test.) Somewhat later, Freundlich and Lindau[5] working with colloidal iron oxide have shown that the flocculation values for sodium chloride increase with increasing hydrogen-ion concentration of the sol. Their method was to alter the PH of the system by adding different concentrations of sodium acetate–acetic acid buffers. Mukherjee and Sen,[6] experimenting with an arsenious sulfide sol, account for the large flocculation value of salts with organic ions as being due to increased OH–-ion concentration from hydrolysis, the hydroxyl ion serving to charge the colloidal particles more negatively.

In cases under Groups 1, *2* and **5**, the charging property of the hydrogen ion on colloidal ferric oxide is shown clearly since the stability as measured by flocculation data increases as the acid concentration becomes greater The same is true in Group 6, which includes the trivalent ferricyanide and phosphate ions. Here again we see that the flocculation value increases with increasing acidity. However, an anomaly is encountered when the electrolytes in Group 4 are considered. The flocculation values of potassium sulfate, ammonium sulfate and calcium sulfate decrease with increase in H^+-ion concentration. The decrease in stability in this case is a well-defined, reproducible phenomenon. To avoid any possibility of error in observation of the peculiar conduct of these electrolytes, the experiment has been checked repeatedly using very pure reagents. The results have been the same. At present there is no available explanation for such an unexpected behavior. It may be mentioned, however, that other investigators have observed somewhat similar, if not related, abnormalities in the coagulation of colloids by ions with different valences. Mukherjee and Sen[6] in studying the stabilizing effect of hydrogen sulfide on arsenious sulfide sols found that whereas it took higher concentrations of monovalent ions to coagulate such sols, they behaved in an anomalous manner when solutions of barium chloride, strontium chloride, magnesium sulfate, and thorium nitrate were used, the sols containing hydrogen sulfide becoming less stable. On the other hand, Ghosh and Dhar[7] have found

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[4] Freundlich, "Colloid and Capillary Chemistry," Methuen and Co., London, **1922, p.** 422.

[5] Freundlich and Lindau, *Kolloid-Z.*, 44, 198 (1928).

[6] Mukherjee and Sen, **J.** Chem. *Soc.,* 115, 461 (1919).

[7] Ghosh and Dhar, **J.** ***Phys. Chem.,*** 30,830 (1926).

that "when a ferric hydroxide sol is coagulated by hydrochloric acid and potassium sulfate, appreciable stabilization takes place because of the adsorption of hydrogen ions. The precipitation value of potassium sulfate with ferric hydroxide sol is 0.10 millimoles per liter when no acid is present. In the presence of 0.1 cc. of *N*/500 hydrochloric acid the precipitation value becomes 0.15 mml. On further increasing the concentration of acid it is found that the precipitation value of potassium sulfate remains constant when 0.3, 0.4 or 0.5 cc. of *N*/500 hydrochloric acid is added." A comparison of their results, on a sol prepared by the Krecke method follows. Both sols had approximately the same concentration.

Ghosh and Dhar		Hazel and Sorum	
Concn. of HCl after dilution	**F. V., mm./l.**	**Concn. of HCl after dilution**	**F. V., mm./l.**
0	0.10	0	0.125
N/30000	.15	*N*/25000	.12
N/15000	.167	*N*/10000	.11
N/10000	.175	*N*/5000	.10
N/7500	.175	*N*/2500	.09
N/6000	.175	*N*/1000	.08

The agreement is not good and will have to be charged to the complex nature of the system with which we are working.

The potassium ferrocyanide data are for flocculation of a positive sol. Higher concentrations of this electrolyte recharge a positive ferric oxide sol to the negative form and it is thus possible to obtain an irregular series. A later paper will include the relation of the irregular series to H^+-ion concentration of the sol.

Summary

1. The stability of colloidal iron oxide has been shown to be related to the H^+-ion concentration of the sol.
2. The stability increases with increasing acidity for potassium chloride, potassium bromide, ammonium chloride, barium chloride, potassium chromate, potassium dihydrogen phosphate, potassium ferricyanide and potassium ferrocyanide.
3. Ferric chloride and aluminum chloride hydrolyze to such an extent that the initial P_H of the sol is altered to a constant value, the stability of the colloid being independent of the initial P_H but dependent on the constant value.
4. Sulfates are anomalous in that the sols with lower P_H values are less stable than those of higher P_H values.

MADISON, WISCONSIN

[CONTRIBUTION PROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE POISONXNG EFFECTS OF WATER VAPOR ON THE ADSORPTION OF CARBON DIOXIDE BY MANGANESE DIOXIDE

BY H. W. FOOTE AND J. K DIXON

RECEIVED OCTOBER 7, 1930 PUBLISHED JANUARY 12, 1931

Manganese dioxide, when pure, catalyzes the reaction between carbon monoxide and oxygen to form carbon dioxide. Water vapor is a strong poison for this reaction, making the oxide inactive.[1] It has been shown that water is adsorbed by manganese dioxide and that, when the pressure is less than about four tenths the saturation value, the adsorption is a surface phenomenon.[2] Water vapor must retard the oxidation of carbon monoxide by covering a part of the surface of the oxide which is available for the adsorption of the reacting gases. The present paper deals mainly with the effects of the presence of water on the adsorption isotherms of carbon dioxide on manganese dioxide at 25°.

Materials, Apparatus and Experimental Procedure

The manganese dioxide used is from the lot prepared and used in previous work.[2] Carbon dioxide, from a tank, was dried by passing through concentrated sulfuric acid and over phosphorus pentoxide.

The apparatus used for determining the adsorption isotherms was of the constant volume type.[3] A small bulb of known volume (20–22 cc), containing the oxide, was connected to a forevolume of known capacity. Gas at a known pressure and temperature in this forevolume was allowed to expand into the adsorption bulb. The oxide adsorbed the gas and the pressure decreased. The pressure decrease was a measure of the amount of gas adsorbed, if correction were made for expansion of the gas into the adsorption bulb. The changes in temperature in the forevolume were noted, the appropriate corrections being applied for these variations.

The apparatus was constructed of pyrex glass. The adsorption bulb was maintained at 25° by means of a large water thermostat. The forevolume contained a McLeod gage, a U-tube for measuring pressures above 2 mm., a bulb of suitable size, and connections to the vacuum pumps and gas generating system. The mercury in the U-tube and McLeod gage was maintained at fixed levels. When the mercury was at these levels, the capacity of the forevolume was known from previous calibration by means of mercury or water.

About 4 g. of manganese dioxide was weighed into the adsorption bulb and, in all experiments, then heated at 190 ± 3° for three hours under the vacuum produced by a mercury pump backed by an oil pump. The oxide was cooled and immersed in the thermostat. The gas under investigation was admitted to the forevolume and its pressure and temperature noted, after the system had been swept out several times. This gas was admitted to the oxide and its pressure and temperature determined at regular time intervals until the pressure attained a constant value. This was taken as the equilibrium point. The stopcock to the adsorption bulb was closed, more gas

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[1] Rogers, Piggot, Bahlke and Jennings, THIS JOURNAL, **43, 1973 (1921); Whitesell** and Frazer, *ibid.*, **45, 2841 (1923);** Lamb and Vail, *ibid.*, **47, 123 (1925).**

[2] Foote and Dixon, *ibid.*, **52,2170 (1930).**

[3] See, for example, Hoskins and Bray, *ibid.*, **48,1454** (1926).

admitted to the forevolume, and the next equilibrium point measured in the same way as before.

The surface of the oxide was poisoned with a known amount of water as follows. The forevolume was filled with water vapor up to any desired pressure and its temperature recorded. Connection with the oxide, which had just been outgassed, was made and the vapor was adsorbed, leaving a negligible amount in the gas space. It was necessary to repeat this process several times whenever the amount of water desired corresponded to a pressure in the forevolume greater than the vapor pressure at room temperature.

The weight of outgassed oxide has been used to calculate the amount of gas adsorbed per gram of oxide. In previous work[2] the weight of oxygen and watrr lost by a sample of oxide during heating was determined by direct weighing. The mean of thirteen experiments showed that the loss in weight was practically constant and equivalent to **0.0379** g. per gram of original oxide. The volume of the adsorption bulb was corrected for the volume of the outgassed oxide, the specific volume of the oxide being taken as 0.2168 cc. per gram.'

The equilibrium pressure extended from **3** to 500 mm. of mercury. Since the object was to compare the isotherms for a poisoned and unpoisoned oxide, no attempt was made to read the pressures closer than **0.1** mm. The largest capacity of the forevolume was 821 cc. and the pressure changes in this volume were never less than **5** mm. The results given in the following sections are accurate to 4% or better.

The Adsorption Isotherms of Carbon Dioxide

The capacity of the forevolume in the experiments was 821 cc. The adsorption isotherms of this gas on manganese dioxide at 25° are plotted in Fig. 1, v/m as ordinate and p as abscissa. v/m is the number of cubic centimeters of carbon dioxide, reduced to 0° and 760 mm. pressure, adsorbed per gram of outgassed oxide, and p is the equilibrium pressure in millimeters of mercury. Curve 1 represents the isotherm for an oxide unpoisoned with water vapor. The amount of water necessary to cover the surface of one gram of oxide at 25° we assume is approximately 0.063 g. This assumption is based on the adsorption isotherm of water on manganese dioxide at this temperature.? The weight of water used to poison the oxide of Curve 2 was 0.0096 g. per gram of oxide, or 15% of the surface was covered. In Curves **3** and 4, 34 and **38%** of the surfaces were covered, respectively.

The results show that when approximately 35% of the surface is covered with water vapor, the amount of carbon dioxide adsorbed is reduced by about 50%, the effect being more pronounced at lower pressures. This is a strong indication of the presence of active adsorption patches on the oxide. Since the water covers these patches, the adsorption of carbon dioxide shows a greater decrease than we would expect from the fraction of the surface poisoned.

The small amount of water used in these experiments is adsorbed so completely from the vapor phase that it is very unlikely that carbon dioxide can displace it from the solid to a measurable extent. If it were displaced,

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[4] Draper, THIS JOURNAL, 50, 2637 (1928).

however, the surface covered by water vapor would be less than calculated without decreasing the partial pressure of carbon dioxide proportionally and the effect would be even more pronounced than stated above.

Two check runs in the absence of water vapor agree with Curve 1. The adsorption and desorption curves nearly coincide at all pressures. The time necessary to attain equilibrium was ten minutes, although readings were taken over a period of one hour. The manganese dioxide of Bray and Hoskins[3] adsorbed only about half the amount of carbon dioxide that we have found for our sample of manganese dioxide, the attainment of equilibrium was slower, and adsorption somewhat irreversible.

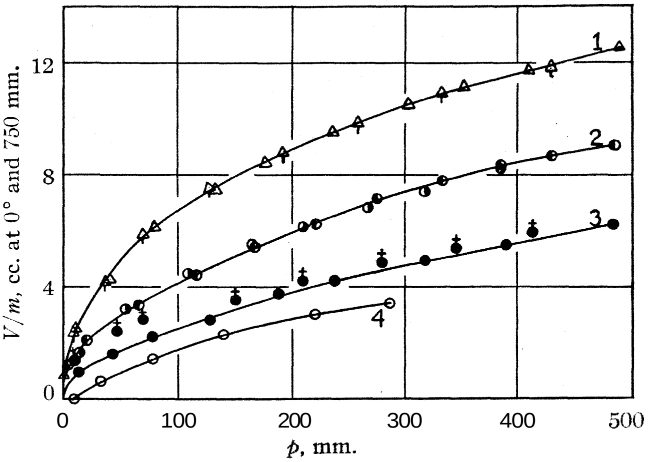

Fig. 1.—Effect of water on the adsorption isotherms of carbon dioxide on manganese dioxide at 25°. % of surface poisoned with water: 0 %, A adsorption, △ desorption; 15%, ◐ ads., ◑ des.; 34%, ● ads., ● des.; 38%, ○ ads.

The Behavior of Carbon Monoxide toward Manganese Dioxide Containing Adsorbed Water.—It is well known that carbon monoxide reacts with manganese dioxide at room temperature to form carbon dioxide and the latter may then leave the surface.[5] However, the carbon monoxide may form manganese carbonate or, after reaction, the carbon dioxide formed may remain in the form of the carbonate.[6] Whether this behavior is to be classed as true adsorption may be questioned. The isotherms have the general form of adsorption isotherms, however, and we shall so refer to them. Since the system carbon monoxide–manganese dioxide is so complicated, we shall report only qualitative results, in which it has been assumed that the decrease in pressure in the forevolume is a measure of the carbon monoxide adsorbed. The carbon monoxide used in the experi-

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[5] Benton, THIS JOURNAL, 45, 887 (1923); Hoskins and Bray, Ref. 3.

[6] Frazer and Greider, *J. Phys. Chem.*, **29**, 1099 (1925).

ments was prepared by dropping formic acid into concentrated sulfuric acid. It was then purified by passing it over solid potassium hydroxide, through concentrated sulfuric acid and over phosphorus pentoxide.

The adsorption and desorption isotherms of carbon monoxide at 25° were determined for samples of oxide poisoned and unpoisoned with water vapor. The pressure did not attain a constant value, after any new addition of gas, even at the end of four hours, but this further decrease in pressure was slow. Four to five hours were allowed for the system to reach this nearly steady state which was taken as an arbitrary equilibrium point.

The isotherms are highly irreversible, about 50–60% of the gas being retained very strongly by the oxide. The adsorption isotherms are of the same shape as those for carbon dioxide (see Fig. 1), but the amount of carbon monoxide adsorbed is approximately twice as great for the same pressure. The adsorption on a surface of oxide poisoned with water vapor is similar to that of carbon dioxide, especially below 250 mm. pressure. That is, the first fraction of the surface poisoned causes the greatest lowering of adsorption. Further poisoning decreases the adsorption, but by no means in a strictly proportional manner.

Summary

The adsorption isotherms at 25° of carbon dioxide on manganese dioxide with and without adsorbed water have been determined. The adsorption is reversible. Water reduces the adsorption markedly. The results indicate the presence of "active adsorption patches" on the oxide surface since the first portion of water adsorbed results in the greatest lowering of the carbon dioxide adsorbed.

The corresponding behavior of carbon monoxide toward manganese dioxide with and without adsorbed water is more complicated. Adsorption is highly irreversible, but the presence of adsorbed water causes the same qualitative effect that it does with carbon dioxide.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

DIFFUSION OF ELECTROLYTES, RON-ELECTROLYTES AND COLLOIDAL ELECTROLYTES[1]

BY JAMES W. MCBAIN AND TSUN HSIEN LIU

RECEIVED OCTOBER 10, 1930 PUBLISHED JANUARY 12, 1931

Diffusion is one of the simplest and most fundamental properties of substances in solution and yet its characteristics are seldom adduced even in discussing such closely allied phenomena as electrical conductivity or its dependence upon concentration. Surprise at this neglect largely disappears when the meager and somewhat conflicting data collected in "International Critical Tables" and in Landolt–Bornstein–Roth are scrutinized and when it is recalled that each number there recorded is the result of prolonged and laborious experiment dependent upon the most painstaking precautions, each result being independent and therefore of no assistance in obtaining further data. Hence, in some instances, the data are conflicting even as regards the sign of the effect of a single factor such as concentration.[2]

The first necessity is therefore to obtain a method by which data that are fully comparable with each other may be readily obtained. It will be shown that standardization of the method recently developed by Northrop[3] enables it to yield results in twenty-four hours that are readily reproducible to within a few tenths of a per cent. and that are thus favorably comparable with those of the laborious classical methods, while exhibiting the further advantage that they permit a ready study of the effect of such factors as viscosity, concentration or admixtures upon rate of diffusion of any one substance. It is shown that the diffusion of electrolytes diminishes to a significant extent with increase of concentration and that the reasoning employed in the discussion of electrical conductivity by Debye, Hückel and Onsager leads to the conclusion that this is in direct proportion to the ratio of the actual osmotic pressure to that at infinite dilution.

The Nernst equation, which applies only to the diffusion of electrolytes at extreme dilution, and the Einstein equation, which applies only to uncharged colloidal particles and large spherical molecules, are generalized and combined to a single equation which appears to hold good for all concentrations, even for such a complex case as solutions of soap, which are crystalloidal when dilute and contain two kinds of colloidal particles when more concentrated. The ready production of new data facilitates the

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[1] Experiments by T. H. Liu.

[2] For example, taking from Landolt–Bomstein–Roth the data for potassium chloride, perhaps the most carefully studied electrolyte, Öholm at 18° finds for 0.01, 0.1 and 1.0 *N*, 1.46, 1.39 and 1.33, respectively, whereas, on the contrary, Thovert at 17.5° obtains for 0.02, 0.1 and 0.9 N, 1.36, 1.38 and 1.52, respectively. Schulmeister obtained 1.10 for 1.3 N at 10°, but Graham–Stefan found 1.41 for 1.26 N at only 12.5°.

[3] J. H. Northrop and M. L. Anson, J. Gen. *Physiol.*, 12,543 (1929).

examination of many interesting problems such as the dimensions and solvation of molecules and colloidal particles in solution, the great difference found between the gross viscosity of a system and that which determines its diffusion or conductance, and the effect of the simultaneous diffusion of various substances upon each other. For example, it is shown that different substances do not diffuse independently, but that one may construct a liquid diffusion pump whose action is analogous to that of the ordinary gaseous diffusion vacuum pump.

Experimental Method

Northrop's method consists in separating two homogeneous bodies of solution by an indifferent membrane with pores of visible or microscopic size, confining the diffusion gradient to within this membrane. Membranes of alundum and of sintered glass have been used. We have found it advantageous to buy cells direct from the Jena Glasswerke[4] in order that the sintered glass may be fused directly to the remainder of the cell. The pore diameter which they designate as G-4 has proved most suitable, and for our purposes the cells required no alteration before use except to grind away the slightly projecting edge of the glass. The cell is shown in Fig. 1 dipping into a closely fitting beaker of water. We have found that the detailed procedure given in the following paragraph enabled us to obtain the results already indicated without any elaborate precautions for the avoidance of vibration or extreme constancy of temperature. The results are necessarily relative but are standardized, as in using a conductivity cell, by a measurement of a single standard solution such as 0.1 *N* potassium chloride, of which the absolute value is already established.

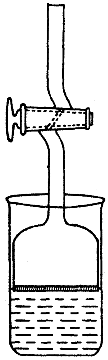

Fig. 1.—The diffusion cell.

After testing for leaks, the volume of the diffusion cell up to the glass stopcock is determined by weighing. It is then suspended by a 5-mm. rubber tube about 15 cm. long and the suspension or stem adjusted until the diaphragm is accurately horizontal as tested against a large mercury surface. This is to minimize the possibility of streaming through the diaphragm. The cell is first cleaned by sucking cleaning solution through the porous disk, using a water pump at the upper end. The liquid is expelled again by applying a pressure of not more than one meter of water. After thorough rinsing, water freed from dissolved gas by boiling or shaking in vacuo is drawn through the diaphragm in order to dissolve any air therein. Bubbles are dislodged by sudden increase in suction, which may serve as a test for the removal of air. In removing the water the pressure is released just as the last layer is about to enter the diaphragm.

The solution to be investigated is freed from dissolved gas by boiling for a few minutes at room temperature in the vacuum of a good water pump. The cell is then rinsed and charged with the solution through the diaphragm and filled completely,

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[4] Schott und Gen., Jena, Germany; American agent, J. E. Bieber, 1123 Broadway, New **York** City.

without bubbles, past the stopcock which is then closed. The cell is first immersed in a large beaker of pure, gas-free water, and before placing it in the surface of the beaker of gas-free water shown in Fig. 1, the last drop of adherent water is removed by slightly tilting the diaphragm and touching it with a glass rod

The preliminary diffusion proceeds for a few hours or whatever time is necessary to establish a steady diffusion column within the disk. This can be calculated from the time required for that part of the solution which is within the diaphragm to diffuse out entirely; for hydrochloric acid about two hours is required Finally, the cell is transferred, after removal of adherent liquid as before, to a clean beaker containing a quantity of gas-free water equal to the volume of the cell The space between cell and beaker is closed with a ring of rubber dam to minimize evaporation. The measurement now begins. The preliminary diffusion not only creates the uniform diffusion gradient within the diaphragm but enables the solutions to attain the temperature of the thermostat in which the apparatus is placed.

After sufficient diffusion has occurred to permit of an accurate analysis of the dilute solution formed in the beaker, the cell is removed and wiped with filter paper, including the inside of the tubing above the stopcock. The solution is extruded through the diaphragm, the first 10 cc. or so being discarded and a sample of the remainder being taken for analysis.

We have made use of cells whose diaphragms had the following characteristics:[5]

Material	Trade designation	Approximate pore radius, Å.	Diameter and thickness, cm.
Glass	G-3	$(15\text{–}20) \times 10^4$	5×0.3
Glass	G-4	$(2\text{–}5) \times 10^4$	$5 \times .2$
Alundum[6]	RA225	$(8\text{–}10) \times 10^4$	$5 \times .2$
Alundum	RA98	$(10\text{–}15) \times 10^4$	$5 \times .2$

The glass diaphragms allow faster diffusion than those of alundum. Diffusion in the finer glass diaphragm is as fast as in the coarser one, while the possibility of streaming is eliminated. It will be noted that the pores have about ten thousand times the diameter of such large molecules as sucrose and one or two thousand times the diameter of hemoglobin or the smaller particles of blue gold.

Method of Calculation.—From Fick's equation for the amount ds diffusing per interval of time dt

$$ds = DA\frac{dc}{dx}dt$$

where D is the diffusion coefficient and A the effective area of all the pores. The diffusion gradient, dc/dx, being linear within the disk, may be set equal to $\Delta x/\Delta x$, where Δx is the thickness of the disk, whence $ds/dt = DA.\Delta c/\Delta x$ and since the volume V of water in the beaker is equal to that in the cell, $ds/dt = D(A/\Delta x)(c_0 - 2c)$, where c_0 is the initial concentration and c is the concentration to which the solution in the beaker has attained and

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[5] The pressure required to force air bubbles freely through the diaphragms under water confirmed the radii ascribed to the alundum disks but indicated slightly smaller values than those here given for the glass diaphragms.

[6] Norton Co., Worcester, Massachusetts.

where $c = s/V$. Hence, $dc/dt = Dk'V(c_0 - 2c) = Dk''(c_0 - 2c)$ where k' and k'' are constants. Therefore, ln $(c_0 - 2c) = -2Dk''t + \text{const.}$ Therefore

$$KD = \frac{\log_{10} c_0 - \log_{10}(c_0 - 2c)}{t_E}$$

where K may be entitled the cell constant, t_E is the elapsed time, and c is 0 at the beginning of the experiment if the diffusion is taking place into water. By measuring the diffusion of a standard substance such as 0.1 N potassium chloride, whose diffusion coefficient is known[7] to be 1.448 at 20°, the cell constant K is determined and all diffusion constants D measured with that cell are expressed in absolute values.

Critical Tests of the Experimental Method.—Northrop[8] states that "hydrochloric acid, lactose and several salts were used" and that "the same cell constant was obtained." He applied his cell to the determination of the molecular weight of carbon monoxide hemoglobin, which he found to be 68,500 ± 1000. At first sight this appears highly satisfactory, but actually there is a glaring and unexplained discrepancy with the diffusion observed by Svedberg and Nichols[9] in the ultracentrifuge, which yielded a value of 113,000,[10] from which it was deduced that hemoglobin particles could not be spherical. Hence it is necessary to scrutinize the method more closely.

A. Homogeneity of the Solutions in Cell and Beaker.—Mechanical stirring introduces much more error than it obviates. Mixing is largely automatic since the heavier portion of the solution overlies the lighter portion in both cell and beaker. Imperfect mixing would be revealed in a change of the value of KD with longer elapsed time and might be greatest for fast diffusing substances such as hydrochloric acid. However, the following is the consistent series of data obtained at 20.5' for 0.5 N hydrochloric acid after the experimental procedure described above was adopted. Cell F used in these six experiments had a capacity of 91 cc., and the hydrochloric acid was determined by titration. The second and third columns are the number of cubic centimeters required to titrate the whole of the diffused hydrochloric acid and the number of cubic centimeters to titrate 25 cc. of the solution recovered from the cell, respectively. It is the ratio of these numbers rather than their absolute values which appears in the calculation.

Similarly, values of *KD* equal to 274 and 272 were obtained in cell B for 0.4 N acetic acid when the times were sixty-three and forty-one hours, re-

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[7] E. Cohen and H. R. Bruins, *Z. physik. Chem.*, 103, 404 (1923); 113, 157 (1924).

[8] J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, 12, 549 (1929).

[9] J. B. Nichols, "Colloid Symposium Monograph," The Chemical Catalog Co., Inc., New York, 1928, Vol. VI, p. 296.

[10] Nichols made the obvious error of inverting the ratio in his arithmetic and writes 41,000 instead of 113,000.

TABLE I

DIFFUSION OF 0.5 *N* HYDROCHLORIC ACID AT 20.5°

t_E, hours	c	c'	KD
19.90	20.22	35.52	688
31.04	20.70	34.42	687
20.97	20.75	34.56	689
40.07	44.85	40.18	686
16.43	16.70	35.50	687
9.20	9.86	37.30	687

spectively. Likewise, for 0.1 *N* potassium chloride with two different methods of analysis KD was equal to 407 and 409 in cell F when the times were forty-two and twenty-five hours, respectively. Finally, the ratio between the diffusion coefficients for 0.1 *N* potassium chloride at 20° and 1.0 *N* sucrose at 25° was 3.79 by this method as compared with 3.82 from Öholm's data.

B. Temperature Expansion.—A fortuitous alteration of temperature by 0.2° would cause an expansion of only 0.006% and cause an absolute error of 0.038% in such an experiment as the first in the table just cited.

C. Streaming through the Diaphragm.—With a fine glass diaphragm such as that employed in cell F it requires seventeen minutes to force through 91 cc. of 0.1 N potassium chloride using a pressure of 85 cm. of water. From this it follows that if there is an inaccuracy of 0.2 mm. in leveling the diaphragm, the flow in twenty-four hours will be about 0.006 cc., causing an error of 0.06% in the result. A sugar solution would be heavier but much more viscous. Another effect of gravity might be sedimentation; this is quite negligible for molecules but for gold particles of 50 Å. radius it might be 4.6% as great as diffusion.

D. The Nature of the Diaphragm.—The most important question that arises with regard to this method of measuring diffusion is whether or not the neighborhood of the extensive surfaces within the diaphragm affects the nature or extent of the diffusion. In the first place, the high mobility of substances upon a solid or liquid surface exposed to a gaseous phase must here be lacking where the solid is immersed in a liquid and the whole space is close-packed with matter. The second conceivable possibility is in the opposite direction and has to be considered more seriously. It is that the surfaces may tend to suppress diffusion through the orientation and immobilization of the adjacent solvent molecules Even if this does occur, and even if it extends to a thickness of many molecular diameters, it might be largely obscured by the fact that the average pore diameter is of the order of 10,000 molecular diameters, and it would completely disappear from the results if the effect were the same upon different solutes. The only way of testing the effectiveness of this or any other specific action of the various diaphragms is by seeing if they give the same numerical result independent of whether glass or alundum is used and of whether the pores are coarse or fine, and by comparing such results with those of the classical methods. For this purpose the following results are adduced.

Cells B, F and G were of fine alundum, glass (G-4), and coarse alundum, respectively, and their cell constants were 294.3, 282.0 and 185.0, respectively. Hydrochloric acid was determined by titration, whereas potassium chloride and sucrose were measured by the Zeiss interferometer, having first prepared a (straight line) graph of interferometer reading against concentration with known solutions. More concentrated solutions were diluted before using the interferometer.

TABLE II

DIFFUSION WITH DIFFERENT DIAPHRAGMS

Solution	Temp, °C.	Cell	t_E, hours	c	c'	KD
0 05 N sucrose	25	F	24.87	139	178	129 6
05 N sucrose	25	F	30.60	157	177	129.8
4 N HCl	21	F	19.03	21.63	39.35	696
4 N HCl	21	F	19.38	22.05	39.25	696
.1 N KCl	20	F	41.97	248	177	406
.1 N KCl	20	F	25.27	18.85	43.63	409
.1 N KCl	20	F	27.60	20.23	43.07	408
05 N sucrose	25	B	24.52	137	177	135.5
.4 N HCl	21	B	19.18	21.05	39 20	729
4 N HCl	21	B	18.80	20.87	39.30	728
.1 N KCl	20	B	29.00	203	179	425
.1 N KCl	20	B	25.42	18.32	43.40	427
.05 N sucrose	25	G	25.25	111	181	85.2
.05 N sucrose	25	G	30.85	123	181	85.4
.4 N HCl	21	G	19.23	14.63	41.65	457
.4 N HCl	21	G	19.57	14.90	41.70	457

When the above data are compared in various ways, it is seen that the results appear to be independent not merely of the diaphragm but of the method. For example

$$\frac{KD\text{ for }0.4\ N\text{ HCl in "F"}}{KD\text{ for }0.4\ N\text{ HCl in "G"}} = 1.524\text{ and }\frac{KD\text{ for }0.05\ N\text{ sucrose in "F"}}{KD\text{ for }0.05\ N\text{ sucrose in "G"}} = 1.520$$

$$\frac{KD\text{ for }0.4\ N\text{ HCl in "B"}}{KD\text{ for }0.4\ N\text{ HCl in "G"}} = 1.593\text{ and }\frac{KD\text{ for }0.05\ N\text{ in sucrose "B"}}{KD\text{ for }0.05\ N\text{ in sucrose "G"}} = 1.588$$

$$\frac{KD\text{ for }0.4\ N\text{ HCl in "F"}}{KD\text{ for }0.1\ N\text{ KCl in "F"}} = 1.709\text{ and }\frac{KD\text{ for }0.4\ N\text{ HCl in "B"}}{KD\text{ for }0.1\ N\text{ KCl in "B"}} = 1.708$$

The diffusion coefficients of 0.05 *N* sucrose at 25° in cells B, F and G are 0.461, 0.460 and 0.461, respectively; whereas Öholm's values corrected for temperature and viscosity by Einstein's equation would be 0.457. Similarly, for 0.4 N hydrochloric acid at 21° they are 2.476, 2.473 and 2.470, respectively, as compared with Öholm's corrected value, 2.43. Again, the ratio of the diffusion constant here found for the hydrochloric acid to that found for the sucrose is 5.37, whereas from Öholm's corrected data 5.31 would be predicted.

Theoretical Formulation of Diffusion **Data.**—Nernst,[11] on the basis of the close connection between the forces giving rise to diffusion and osmotic pressure, derived the well-known equation for electrolytes in extreme dilution

$$D = \frac{2RT}{\frac{1}{U} + \frac{1}{V}}$$

where U and V are the ionic mobilities at infinite dilution as measured by electrical conductivity. Thus for an electrolyte whose ions have the same mobility at 18°, $D = 0.02243U$. This last expression is applicable to neutral molecules or colloidal particles of the same size as an ion of mobility U or V. In this way Nernst could estimate the approximate diffusion coefficients of neutral molecules or un-ionized electrolytes. Haskell's[12] formula is an expansion of that of Nernst for the diffusion of electrolytes which dissociate into ions of unequal valency.

The other theoretical contribution is that of Einstein[13] for uncharged spherical particles or molecules very large in comparison with those of water

$$D = \frac{RT}{N6\pi\eta r}$$

where r is the radius of the particle, η the viscosity of the medium and the denominator is the sum total of the resistance to movement of each of the particles calculated by Stokes' law.

It is evident that the numerators of the Nernst and Einstein equations are alike in containing the osmotic term RT for each molecular species. Likewise, their denominators contain the sum total of the resistances to movement.experienced by the different ions, molecules and particles present. We may therefore generalize the reasoning which Nernst and Einstein have applied to these two particular cases and write in the numerator the actual osmotic term iRT and in the denominator the sum of all the resistances to motion of the ions, molecules and particles evaluated by whatever methods are available in each case. Hence

$$D = \frac{iRT}{\text{sum of resistances}} = \frac{iRT}{\Sigma(1/U_m)}$$

where $1/U_m$ is the resistance to movement of a particular species and is also equal to RT/D_m where D_m is the diffusion coefficient of that molecular species.

For example, for an incompletely dissociated uni-univalent electrolyte, such as potassium chloride may be at higher concentrations, the diffusion coefficient at any concentration is given by the formula

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[11] W. Nernst, *Z. physik. Chew., 2, 613 (1888);* "Theoretische Chemie," 10th ed 1921, pp. 425431.

[12] R. Haskell, *Phys. Rev.,* [1] 27, 145 (1908).

[13] A. Einstein, *Z. Elektrochem.,* 14, *235* (1908).

$$D = \frac{iRT}{\alpha\frac{1}{U} + \alpha\frac{1}{V} + (1 - \alpha)\frac{1}{U_{\mathrm{KCl}}}}$$

The Diffusion of Electrolytes.—The Debye–Hückel–Onsager[14] theory is an analysis of the chief forces acting upon free ions in aqueous solution. They enumerate three whose sum should determine the electrical conductivity of the solution. The first is that due directly to the electrical charge overcoming ordinary friction and is represented by the mobility at infinite dilution. The second, which diminishes the conductivity, is unfortunately termed the electrophoretic force and represents the opposing effects of the viscous drags of the two clouds of ions moving through the same solution in opposite directions. The third likewise tends to lower the conductivity and is called the electrical force of relaxation and is due to the fact that any movement of an ion must be followed by a slight alteration in the distribution and arrangement of all surrounding ions. The result of the last two terms is that the conductivity A at any concentration is given by the expression A = **A,** $- \Lambda_{\mathrm{I}} - \Lambda_{\mathrm{II}}$ so that the conductivity diminishes with increase in concentration if ionization remains **100%** complete.

Now diffusion is simpler than electrical conduction. The prime force acting upon an ion is that represented by the osmotic term RT as driving force and by $1/U_\infty$ as resistance. The second influence enumerated by Debye and Hückel, namely, the opposing viscous drags of the ions when moving past each other in opposite directions, is here essentially eliminated because all ions are moving in the same direction. The negligibility of this effect is most obvious for a case such as potassium chloride where both ions are equally fast but it is likewise true of all other simple electrolytes because after the first few moments in which the Nernst diffusion potential is set up, equal amounts of both ions are diffusing together. Onsager[15] has expressed a similar opinion for such electrolytes as potassium chloride. Cataphoretic forces then will not intervene to lessen the movement of ions with increase of concentration.

The third force envisaged by Debye and Huckel is due to the relaxation or alteration in the distribution of the ionic atmosphere whenever an ion is displaced. It may not be entirely eliminated in diffusion but it is certainly minimized when, as here, we have a linear diffusion gradient and all the ions are traveling in the same direction. What is happening is a uniform dilution of the ionic atmosphere and this is minimized when, as in some of our experiments, the diffusion takes place, not into pure solvent, but only into a slightly less concentrated solution.

The net result is that in diffusion the denominator of our generalized

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[14] **P. Debye and E. Hiickel,** *Physik.* **Z., 24, 305 (1923); L. Onsager,** *ibid.*, **27, 388 (1926); 28,277 (1927).**

[15] **L. Onsager,** *Trans. Faraday Soc.*, **23,356 (1927).**

equation, representing the forces opposing movement, remains appreciably constant as long as the ions are not changed or replaced. This leaves the observed decrease with concentration to be explained primarily by the change in the effective osmotic pressure as given in the numerator.

The diffusion data that we have obtained for potassium chloride are given in Table III. The cell constants were obtained from measurements of 0.1 N potassium chloride at 20°, giving values of KD for cell *G-3* of 503, 501 and 504, and for cell G-4 of 481,480 and 484; whence the cell constants are 348.0 and 332.7, respectively.

TABLE III

DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE AT 25°

Concn., N	Cell	t_E, hours	c	c'	KD	D
0.02	B	20.47	119.6	122.4	500	1.698
.02	F	21.67	120.0	123.2	477	1.672
.02	*G-3*	22.75	134.3	121.0	588	1.691
.1	G-3	35.82	37.40	41.70	568	1.631
.5	F	30.30	21.25	39.14	445	1.580
.5	B	28.68	20.15	39.10	466	1.567
.5	G-4	23.46	22.75	39.25	524	1.572

It is possible to account for these data as **a** first approximation within less than 2% by using the simplified formula $D = iRT/(1/U + 1/V)$, in which it is assumed that only the numerator changes while the denominator remains constant. This assumption will be referred to briefly again. In this way, taking values for i from a table in Taylor's "Treatise on Physical Chemistry" (where i is van't Hoff's empirical ratio between osmotic effect observed and that expected for an ideal non-electrolyte), we derive Table IV for 25°. The same formula would predict at 20° a value of 1.428 for 0.1 N potassium chloride, which is *1.38%* less than that of the standard value of Cohen and Bruins.

TABLE IV

COMPARISON OF OBSERVED WITH PREDICTED EFFECT OF CONCENTRATION FOR THE DIFFUSION OF POTASSIUM CHLORIDE AT 25°

Concn., N	0	0.02	0.1	0.5
D (obs.)	...	1.685	1.631	1.573
D (calc.)	1.721	1.664	1.605	1.544

Other electrolytes likewise exhibit diffusion coefficients at moderate concentrations which are significantly less than those predicted for complete ionization at infinite dilution, D_∞. Some examples of our data at 25° and of Öholm's at 18° are given in Table V.

Inspection of the data in "International Critical Tables" or Landolt–Bornstein–Roth confirms this deficiency in the diffusion constants for moderate concentrations as compared with those predicted by the Nernst equation for infinite dilution, and the greatly increased magnitude of the

TABLE V

COMPARISON OF DATA WITH THOSE OF ÖHOLM

Solution	D at 25°	D_∞ at 25°	D at 18°	D_∞ at 18°
0.1 N HCl	2.674	2.841	2.23	2.43
.5 N HCl	2.663	2.841	2.22	2.43
1 N LiCl	0.985	1.046	0.951	0.994

effect for ternary electrolytes such as potassium sulfate or for solutions where complexes are known to form would appear to substantiate our contention that the chief factor in diminishing the coefficient of diffusion as the concentration is increased is the falling off in the numerator iRT.

There are three current views as to the reason for the decrease in i with increase in concentration. The first holds to 100% dissociation with the attempt to explain all the data by a combination of interionic attraction with other effects. Both the others retain the principles of interionic attraction but one, in the terminology suggested by Bjerrum, assumes 100% ionization but with a larger and larger proportion of the ions "associated to form neutral pairs as concentration increases. The third view, now widely held, is that dissociation is not complete. McBain and Van Rysselberge[16] decided that mere "association" or clustering is insufficient to explain the fact that anionic clusters or complex anions are commonly formed and complex cations are not, whereas the symmetrical operation of electrical forces would produce comparable numbers of both.

The denominator of our general diffusion equation will, of course, seldom remain quite constant with diminishing dissociation on account of the conflicting effects of molecular volume and of hydration or polarization of the solvent by an ion as compared with a neutral molecule. The magnitudes involved cannot be obtained from a direct comparison between the Nernst prediction for acetic acid 1.37 as against the observed value 0.9 on account of the abnormal mobility of the hydrogen ion. It is more pertinent to recall that, as Nernst suggested, for large organic ions the mobility is equal to that of a neutral molecule of the same size.[17]

The Northrop method can equally well be used with non-aqueous solutions. For example, a saturated solution of potassium chloride in 95% ethyl alcohol gave a value for D of 0.817 at 25°. The Arrhenius conductivity ratio indicates 25% dissociation of the potassium chloride, whence by proportion and taking into account the viscosity ratio between alcohol and water, the diffusion coefficient of undissociated chloride in water would be 0.824 if the molecules were identical in the two solvents. The only interest of this approximation is that the resistance to movement of the potassium chloride molecule so indicated is only 4% greater than the sum of those of the potassium and chlorine ions, which is a rough justification of the

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[16] J. W. McBain and P. J. Van Rysselberge, THIS JOURNAL, 52, **2336 (1930).**

[17] For example, T. Svedberg, Z. *physik. Chem.*, **76, 146 (1911).**

assumption of the constancy of the denominator in the equation used for Table IV. A completely non-polar molecule might he expected to have a higher mobility.

Diffusion of Soap as a Colloidal **Electrolyte.**– The surprising range of applicability of our diffusion equation is illustrated by the information yielded for soap solutions, such as potassium laurate at 25°. The proportions of the various constituents for the different concentrations of potassium laurate have been deduced by McBain and Jenkins[18] from conductivity and osmotic data. it will be seen that the diffusion results are in reasonable agreement with the detailed information already available with regard to each of these constituents.

The experimental data are collected in Table VI. To avoid hydrolysis 0.0015 equivalent of potassium hydroxide was added per liter to the more dilute solutions, and the same addition was made to the water in the beaker.

TABLE VI

DIFFUSION OF POTASSIUM LAURATE INTO WATER (0.0015 *N* KOH) AND INTO LESS CONCENTRATED SOLUTIONS OF POTASSIUM LAURATE AT 25°

Soln., N	In beaker	Cell	t_E, hours	c	c′	KD	D
0.025	Water	G-3	23.10	87.0	511	241.4	0.695
.025	Water	G-4	26.65	90.2	509	233.0	.700
,025	Water	G-3	30.07	95.5	504	244.1	.702
.15	Water	G-3	24.00	187	2912	163.7	.470
.15	Water	G-4	23.92	180	2907	155.4	.467
.50	Water	G-4	20.45	377	2373	146.8	.441
.025	Water						.699
.125	0.05 N	G-4	23.00	115	1421	158.0	.475
.3	.2 *N*	G-4	19.70	119	1920	149.0	,447
.5	.4 *N*	G-3	23.41	132	1929	146.8	.421
.5	.35 *N*	G-3	22.12	164	2925	145.1	.417

The experimental values in Table VI are plotted in Fig. 2 together with the point for zero concentration taken from the Nernst equation assuming mobilities of potassium ion as 74.5 and simple laurate ion as 23.2, which gives the value 0.813 at 25°. It will be noted that the diffusion coefficients as measured against water are only slightly higher than those which are confined to a narrower range of soap solution.

Instead of trying to predict independently the diffusion coefficients for representative concentrations, we may examine those found to see if they agree with reasonable expectation. For example, taking first the 0.025 N solution in which potassium laurate is supposed to be a simple electrolyte with no colloid and about 66% dissociated, the diffusion due to the ions should be 0.66 X 0.813 = 0.532. The difference between this and the observed value, 0.699, leaves 0.163 ascribable to potassium laurate molecules. Hence, the diffusion coefficient of the latter is 0.163/0.34 =

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[18] J. W. McBain and W. J. Jenkins, Trans. *Chem. Soc.*, 121,2328 (1922).

0.480, and from the Nernst formula for a molecule $D_m = 0.02243\ U_mT/291$ the value of U_m expressed in electrical units gives a mobility of 20.9 for the potassium laurate molecule. This appears quite plausible when compared with the value of 23.2 for the laurate ion. (The temperature correction 291/298 is the osmotic correction, not that of the mobility)

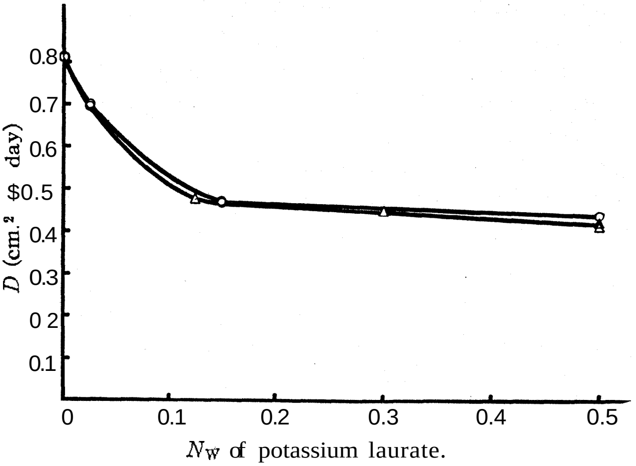

Fig. 2.—Diffusion of potassium laurate at 25°: (a) ○, into water (0.0015 N KOH); (b) △, into less concentrated solutions of potassium laurate.

For 0.5 N potassium laurate there is a wholly different picture in that the soap is now almost entirely in the form of colloid, ionic micelle and neutral micelle. The former is supposed to carry about ten charges and possess a mobility of about 74.5 which is equal to that of the potassium ion. From Haskell's equation we may calculate the diffusion coefficient for a decavalent electrolyte with ten potassium ions to one anion at 25°.

$$D = 0.02243 \times \frac{298}{291} \times \frac{(74.5)^2}{2 \times 74.5} \left(\frac{1}{10} + \frac{1}{1}\right) = 0.941$$

Since only 37% of the solution is in this form, the diffusion contributed by it will be 0.37 × 0.941 = 0.348. That contributed by the 1% of simple ions will be 0.01 × 0.813 = 0.008 and that contributed by the 2% of simple potassium laurate molecules 0.02 × 0.480 = 0.0096. The sum, still omitting that due to the 60% of neutral micelle $(KL)_n$, is 0.366, whereas the total observed is 0.419. This leaves 0.053 for the neutral micelle, whose diffusion coefficient is therefore 0.053/0.60 = 0.088. The significance of this low diffusion constant may be developed by evaluating from it the radius of the neutral micelle according to Einstein's equation for a spherical particle which yields the value 24 Å., or an effective diameter of 48 Å. It is probable that the neutral micelle is not spherical and that its thickness is twice the length of lauric acid, namely, 30 Å. On the other hand, McBain and Jenkins[19] showed by ultrafiltration that its maximum diameter was much less than 150 Å. A real test of this deduction will be possible when we have carried out similar measurements with sodium oleate in which according lo ultrafiltration the neutral micelle is very large.

Returning for a moment to the consideration of the ionic micelle with its ten charges, D = RTU = (0.0230 × 74.5)/10 = 0.171 and the diameter of the ionic micelle equals 0.0883/0.171 × 48 = 25 Å. If the ionic micelle has a radial arrangement, as seems probable, this is less than twice the length of a laurate radical extended to its maximum length, 15 Å., but it is only to be expected that here the chains would coil to a shorter length.

Deductions from the Diffusion Coefficient of Sucrose.—Using cells B, F and G, 0.05 N sucrose at 25° gave diffusion constants equal to 0.461, 0.462, 0.461, 0.462, 0.462; mean, 0.462, as compared with Öholm's 0.457. For 1.0 N sucrose the values 0.381 and 0.376 are obtained with cell G as compared with Öholm's 0.384. This is a remarkable result. The viscosity of these two solutions as determined in a capillary flow viscometer is, namely, 1.047 and 3.080, respectively, times that of water, whereas the diffusion coefficients differ only by 18% in spite of the fact that Einstein's equation predicates that diffusion is inversely proportional to the viscosity.

Evidently, when the increase in viscosity is caused by the diffusing substance, the viscosity correction is definitely not that demanded by Einstein's equation using the viscosity of the solution, but is much less. An explanation may be ventured by picturing that while the increase of the viscosity is due to indiscriminately increased collisions of the large molecule in diffusion when one diffusing molecule of sucrose is hit by another, the retardation of one is often compensated by the acceleration of the other. The situation is reminiscent of that of the closely allied subject of conductivity where it is notorious that the attempt to set it proportional to the first power of the viscosity is an overcorrection. In soap solutions the "viscosity" may vary 1000-fold without affecting the conductivity.

Ulich[21] considered that the reason that many ions have an electrical mobility much greater than corresponds to their supposed size and the viscosity of water, like the small effect which sugar or gelatin or jellies exert upon the electrical mobility of ions, is due to their being very small in comparison with the large molecules such as $(H_2O)_6$ or similarly $(H_2O)_9$, etc. This, however, does not hold in our case where the large molecules of sucrose are unaffected by the high viscosity which they themselves impart.

Calculating the size of the sucrose molecule from its diffusion coefficient in 0.05 N solution, assuming it to be a spherical particle with the density

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[19] J. W. McBain and W. J. Jenkins, Trans. *Chem. Soc.*, 121,2340 (1922).

[20] A. Einstein, ***Ann. Physik,*** [4] 19,289 (1906).

[21] H. Ulich, ***Z. Elcktrochem.,*** 36, 504 (1930).

of solid sucrose, its molecular weight is 388 as compared with its formula weight 342. The difference would be equivalent to a hydration of about two molecules of water.[22]

The Mutual Effect of Diffusing Substances upon Each Other.—It is commonly assumed that substances diffuse quite independently and that they do not influence each other's rate unless they react with each other. Our experiments show that this is by no means true.

Experiments were carried out at 20° with cells B and C, the latter having an alundum diaphragm "RA 228," using 0.5 N hyrochloric acid. First, it was diffused into water, giving values of diffusion constants $D = 2.452$ and 2.448. Next 10% of dextrose was dissolved in the 0.5 N hydrochloric acid and it was diffused into water, giving the values 2.386 and 2.391. Next, 0.5 *N* hydrochloric acid was allowed to diffuse into 10% dextrose in water, giving values of D of only 1.716 and 1.730. Finally, when 10% dextrose was present, both in the hydrochloric acid and in the water into which it was diffusing, the values of D were 2.049 and 2.044. Using an Ostwald capillary viscometer, the viscosity of 10% aqueous dextrose at 20° was found to be 0.01291 as compared with that of water 0.01005, the ratio being 1.283.

Now the ratio of the values of D when dextrose was entirely absent to that when the 10% dextrose was present on both sides of the diaphragm is only 1.196 as compared with the viscosity ratio 1.283. As in the case of sucrose, the viscosity of the solution does not bear a linear proportionality to the effect upon rate of diffusion.

When the dextrose was diffusing with the hydrochloric acid into water, the value of D for the hydrochloric acid was 1.386 times greater than when the dextrose was diffusing in the opposite direction, although the average viscosity and concentration of dextrose must have been nearly the same within the diaphragm in both cases. Hydrochloric acid diffusing alone into water is only 1.025 times faster than when 10% dextrose is diffusing with it. Our explanation is that the molecules in the two diffusing columns bombard each other and thus retard or accelerate each other's motion according as they are opposed or in the same direction.

When the strong acid, hydrochloric, was replaced by the weak acid, acetic, similar effects were produced by the addition of dextrose. 0.5 N acetic acid diffusing alone into water gave $D = 0.929$ and 0.924. When diffusing with 5% dextrose into water the diffusion was, if anything, rather faster, D being 0.929 and 0.927, in spite of the enhanced viscosity. But when the acetic acid alone diffused into 5% aqueous dextrose, the rate was 29% less, D being 0.657 and 0.651.

Dextrose had been used because of its chemical indifference to hydrochloric and acetic acids. Urea is known to combine with acids, its equi-

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[22] Compare J. W. McBain and S. S. Kistler, *J. Phys. Chem.*, 33, 1806 (1929).

librium constant having been measured, and when 0.5 N hydrochloric acid alone was allowed to diffuse into 5% aqueous urea, *D* actually increased from the value 2.450 for water to 2.501 and 2.490 When the 5% urea was diffusing with the hydrochloric acid into water, *D* fell to the much lower values 1.974 and 1.972. The effects are therefore exactly opposite to those where no chemical combination occurs.

Bombardment by the molecules of an indifferent diffusing column may produce an effect which may be called a liquid diffusion pump since it is analogous to that in a gaseous diffusion vacuum pump, To demonstrate this, the cell was charged with 0.5 *N* acetic acid and the beaker with 0.5 *N* acetic acid containing 10% dextrose. After twenty-three hours the concentration of the acetic acid in the cell had increased and that in the beaker had decreased by about −0.6 and +1.0%, respectively. In a similar experiment after forty-seven hours the changes were −1.6 and + 1.8%, respectively. When hydrochloric acid was used instead of acetic acid, in twenty-four hours the changes were −0.4 and +0.7%. On the other hand, when 5% urea was with 0.3 *N* hydrochloric acid in the cell and 0.5 *N* hydrochloric acid alone in the beaker, the changes were in the opposite direction; hydrochloric acid passed from the beaker to join the urea in the cell, the changes being in twenty-four hours \$0.8 and −0.6%.

Other results with ethyl and methyl alcohols suggest that the bombarding effect of a diffusing column may be approximately proportional to the square of its concentration and to the cross-sectional area of its molecules. It is evident that diffusions of more than one substance are not independent of each other. For example, it is not safe to employ buffer solutions without considering the effects here recorded.

Summary

A procedure is given for the use of the Northrop diffusion cell with diaphragm of sintered glass by which very rapid determinations of diffusion may be made reproducible to within a few tenths of a per cent. It is shown that such results are independent of the nature and porosity of the diaphragm and are equal to the best obtained by the laborious classical methods.

The Nernst equation for electrolytes at infinite dilution and the Einstein equation for uncharged spherical particles are generalized to include all cases of diffusion. It is shown that for simple electrolytes the predominant influence is the value of the van't Hoff i factor.

As an instance of the method of summation of the effects due to different constituents in predicting total diffusion, the data for a typical soap solution are analyzed and found to be in agreement with previous information as to their properties. The data for sugar solutions show that the viscosity contributed by the dissolved substance is not that which determines rate of diffusion.

The diffusion column of one substance may, by the bombardment of its molecules, accelerate, retard or even reverse the diffusion of another substance.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE PHOTOELECTRIC PROPERTIES OF AMMONIA CATALYSTS

BY A. KEITH BREWER

RECEIVED OCTOBER 14, 1930 PUBLISHED JANUARY 12, 1931

An extended series of experiments carried out at this Laboratory has shown that **reduced** Fe_3O_4 is an excellent catalyst for the synthesis of ammonia[1] and that the activity is materially influenced by the presence of small amounts of impurities or promoters. A general investigation of the physical properties of these catalysts has been undertaken to determine, if possible, the function of the promoter, as well as add to our knowledge of surface catalysts.

An investigation of the thermionic properties in *vacuo* of a large number of possible catalysts carried out by Dr. C. H. Kunsman[2] has resulted in the discovery that these substances, for the most part, are excellent emitters of positive ions. A comparison of the positive ion emissivities and the catalytic properties[3] showed that no direct relationship existed between different catalysts, although for a given catalyst it is possible that some such correlation does exist.

The present paper deals with the photoelectric properties of several of these catalysts both in *vacuo* and in the presence of nitrogen, hydrogen and traces of oxygen.

The catalysts chosen for this research were described by Almquist and Crittenden[4] and are those which have received the greatest amount of study. The composition and activities of these catalysts are given in Table **I.**

TABLE I

DATA ON CATALYSTS

				% NH_3 at 450°	
No.	Total Fe, %	Al_2O_3	K_2O	30 Atm.	100 Atm
918	72.86	..	..	3.30	5.49
920	72.58	..	0.20	1.57	3.43
921	71.99	1.31	..	5.35	9.35
922	71.99	1.05	0.26	5.80	13.85

The composition percentages are for the unreduced material.

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[1] Larson and Brooks, *Ind. Eng. Chem.,* 18,1305 (1920).

[2] Kunsrnan, J. *Franklin Inst., 204,* 035 (1927).

[3] Kunsman, THIS JOURNAL, 51, 688 (1929).

[4] Almquist and Crittenden, *Ind. Eng. Chem.,* 18, 1307 (1926).

Apparatus and **Method**

A schematic drawing of the apparatus is shown in Fig. I, and is essentially the same as that previously described by the writer.[5]

The catalysts to be tested were coated on platinum filaments in a manner described by Kunsman.[6] Heating above visibility, which might result in sintering or premature fatiguing, was avoided in all except the first coated layer. The filaments were reduced in hydrogen at a temperature between 400 and 450°.

The temperature was measured by means of a platinum–platinum-rhodium thermocouple twisted tightly about the filament.

Commercial hydrogen and nitrogen were used after all traces of oxygen had been removed by glowing tungsten; moisture was removed by liquid air.

A hot mercury arc and a Hilger monochromatic illuminator were used as the source of ultraviolet light. The photoelectric current was measured with a Compton electrometer and high resistance shunt[7] which enabled emission currents to be read from 10^{-15} to 10^{-10} amp.

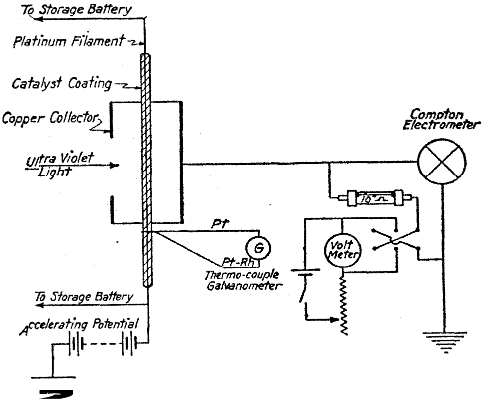

Fig. 1.

The photoelectric threshold was determined by plotting the emission current per unit light intensity against the wave length. The intersection of the curve with the wave length axis is taken as the long wave length limit.

All measurements, unless otherwise specified, were made in the best obtainable vacuum, the pressure at all times being below the sticking point of mercury in the McLeod gage (10^{-6} mm.).

Results

Catalyst 918.—In the study of the coated filament used in these researches the question arose as to the effect of the method of coating on the threshold. A comparison was made, therefore, of a pure iron ribbon and a platinum filament coated with catalyst 918. The results in both cases were substantially the same, showing that the coating process had little or no effect.

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[5] Brewer, *Phys. Rev.*, 35, 1360 (1930).

[6] Kunsman, *J. Phys. Chem.*, 30, 525 (1926).

[7] Brewer, *Rev. Sci. Inst.*, 1, 325 (1930).

The photoelectric threshold for pure but not outgassed iron is given by Hamer[8] as 2870 ± 40 Å. Cardwell[9] gives the threshold for outgassed iron to be very near 2580 Å.

Lines 1 and 2 of Fig. 2 show the results obtained in the present experiments with pure iron. In the figure the wave length in Å. units is plotted against the deflection per unit light intensity expressed in purely arbitrary units, which are different for the various lines. Line 1 was taken with a non-outgassed filament at room temperature and shows a threshold very near 2860 Å., which is in agreement with the value given by Hamer for similar conditions.

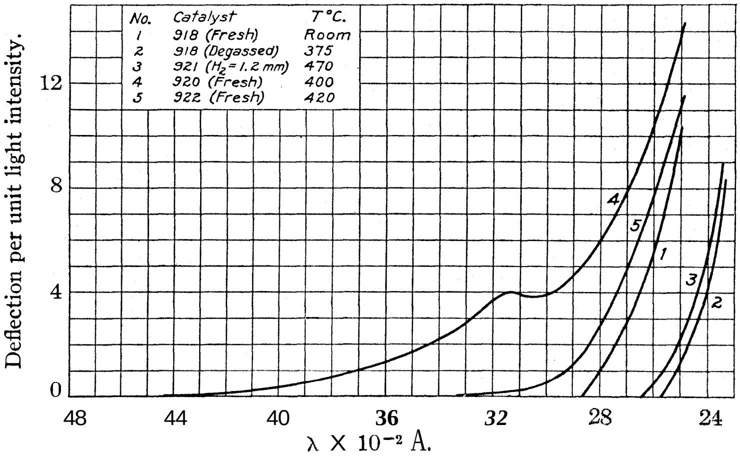

Fig. 2.

The threshold of a fresh filament appeared very sensitive to temperature. Above 200° the threshold started to shift toward shorter wave lengths. After heating at 650° for about twenty-four hours, the threshold shifted to a position as shown by line 2, in which condition it showed a very slight temperature coefficient for temperatures below 700°. The threshold as given by line 2 lies very close to 2575 Å., which is in good agreement with the value given by Cardwell for outgassed iron.

Catalyst 921.—The small quantity of alumina present in 921 had very little or no effect on the threshold as compared to that of pure iron (918). The threshold for the fresh filament was very close to that given by line 1 of Fig. 2, while the degassed filament showed a barely detectable emission for λ2536 Å., and no emission for λ2653 Å.; the threshold, therefore, lies between these two values. The curve itself agreed very well with line 2 of Fig. 2.

Nitrogen and hydrogen had little effect on the photoelectric emissivity,

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[8] Hamer, *J. Opt. Soc.*, **9**, **251** (1924).

[9] Cardwell, ***Proc. Nat. Acad. Sci.***, **14**, 439 **(1928).**

tending to increase the intensity. This effect was most pronounced in the neighborhood of 1 mm. pressure. Line **3** of Fig. 2 is for 921 in hydrogen at 1.2 mm. pressure. It will be noted that the threshold is shifted about 85 Å. to the red over that for vacuum conditions. The effect of nitrogen is very similar to that of hydrogen; oxygen in traces produced no noticeable result.

Catalyst 920.—The positive ion emissivity from the potassium promoted catalyst has been observed by Kunsman[2] to be large hut unstable. This may also be said to be true for the photoelectric emissivity.

The effect of temperature on the photoelectric emissivity was measured for ascending and descending temperatures as well as for the steady state and was found to be quite different from that observed for 918 and 921.

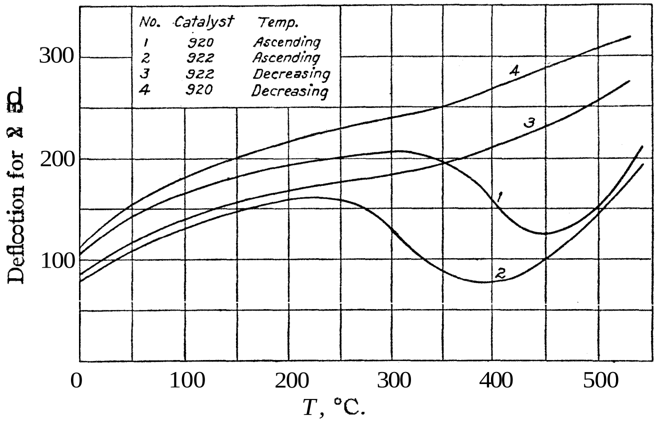

Fig. **3.**

Curve 1 of Fig. 3 for a freshly reduced filament was taken with a rising temperature in which deflection readings were made as quickly as possible after each rise in temperature. It will be seen that the emissivity increased to a maximum in the neighborhood of 300°, followed by a minimum at 450°, and thereafter increased rapidly with temperature. At temperatures just below 600° the photoelectric emissivity became complicated by the thermionic emission of electrons. The approximate photoelectric emissivity up to 700° was measured by placing such a potential on the high resistance shunt that the thermionic current was just balanced out and then measuring the photoelectric current. The results showed little if any increase above 600".

Line 4 of Fig. 3 is for descending temperatures, but otherwise was taken under the same condition as line 1. It will be noted that the pronounced minimum at about 450° is only faintly noticeable.

All experiments on the determination of thresholds were made under steady state conditions, the deflection following line 4 quite closely. At temperatures above 500° these conditions were reached fairly rapidly.

The threshold at room temperature was in the neighborhood of 3200 Å., as only a detectable emission was obtainable with λ3130 Å. As may be expected from Curve 1, Fig. 3, the threshold shifts toward longer wave lengths with rising temperature. Line 4 of Fig. 2 shows the emission per unit intensity at 400° for various wave lengths; emissivity was just detectable at λ4350 Å. and did not occur at A4900 Å.

It will be noted that the characteristics of line 4 are quite different from those of lines 1, 2 and 3. A small maximum is seen at 3100 k., and the foot of the curve, rather than being sharp as is characteristic for pure substances, skirts the wave length axis for a long distance, as is characteristic of composite surfaces.[5]

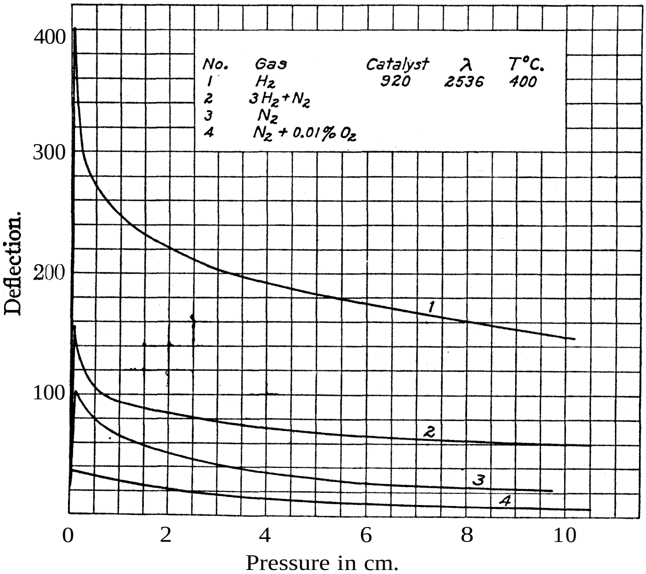

Fig. 4.

The effect of gases on the emissivity is shown in Fig. 4. These runs were taken for A2536 Å. at 400°, and with an accelerating potential of 45 volts.

The emission in hydrogen, nitrogen and the 3–1 mixture of the two gases reached a maximum at about 0.5 mm. pressure. The current intensity was some four times greater in hydrogen than in nitrogen and the 3–1 mixture gave values but slightly higher than did pure nitrogen. Nitrogen containing only a trace of oxygen (estimated at about 0.01%) dropped the emissivity to a point very close to that for pure iron.

Catalyst 922.—The threshold for the cold reduced catalyst is very close to that given by line 1 of Fig. 2 for 918; the K_2O and Al_2O_3, generally considered to be in the form $K_2Al_2O_4$, have but little influence.

The effect of temperature on the emissivity is shown by lines 2 and 3 of Fig. 3, for ascending and descending temperatures, respectively. Line 2 shows a pronounced minimum at 400° which corresponds quite closely to that observed for 920; this minimum is almost completely absent for the descending temperatures.

The threshold of a freshly reduced filament at 420° as given by line 5 of Fig. 2 lies between λ3130 Å. and λ3342 Å. The shape of the curve lies intermediate between that for a pure surface (line 1) and that fur a highly composite surface (line 4), indicating the presence of a small amount of material at the surface with a threshold above that of iron.

In the course of a week's use, in which the filament was repeatedly heated to 500° in nitrogen and in hydrogen and to 700° in a vacuum, the threshold gradually fell to a final value very close to that shown by line 3 for Catalyst 921. This comparatively rapid fatiguing is contrary to what might be expected from the results of Kunsman[2] on the thermionic emission of positive ions, which showed that 922 while not giving as large an initial positive ion emission as 920 is a far more constant source.

Fresh and photoelectrically fatigued filaments were compared, therefore, for positive ion emissivity with the result that the temperature at which an emission became detectable did not increase more than 10° throughout the fatiguing process, although the threshold shifted some 800 Å.

In the presence of gases the photoelectric emissivity of a fresh filament was similar to that shown in Fig. 4 for 920 with the exception that the curves for nitrogen and for hydrogen very nearly coincided. Traces of oxygen had the same pronounced poisoning effect.

In this connection an attempt was made to show the effect of gases on the positive ion emissivity. The problem is complicated because positive ions of the type observed by Kunsman[2] as well as those observed by the writer[10] are both emitted at about the same temperatures. The experiments showed that the temperature at which emission was detected was lowered from 50 to 100° by the presence of a millimeter of gas. Further increases in the gas pressure did not lower the temperature but did increase the current for large accelerating voltages since saturation does not exist in gases, the current becoming proportional to the applied voltage at atmospheric pressure.

Discussion of Results

The thermionic emission in gases from various surfaces is doubtless intimately related to their catalytic properties.[10] This, however, cannot be said for photoelectric emission only in so far as the photoelectric threshold is a measure of the surface forces. Photoelectric emission is generally considered to be confined to the removal of electrons from the emitting

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[10] Brewer, J. Phys. Chem., 32, 1006 (1928).

surface;[5] no satisfactory evidence exists for the emission of either positive or negative ions by this means. Thus these experiments cannot be interpreted to give a direct picture of the mechanism of reaction. Photoelectric emissivity is, however, a sensitive test for the composite nature of surfaces and so may serve to help define a catalytic material.

In the case of Catalyst 918, we see that the long wave length limit agrees exactly with that of pure iron. From this the conclusion can be drawn that the surface forces, image and intrinsic,[10] of the reduced Fe_3O_4 are identical to those of pure electrolytic iron.

The sharp feet of lines 1 and 2 are indicative of the fact that surface is uniform and not composite. Had the emitting material and hence the long wave length limit varied from point to point over the surface, the above lines would have turned off asymptotic to the wave length axis.

The increase in work function, as is shown by the shift in threshold from 2860 Å. to 2580 Å. during the outgassing process is characteristic of photoelectric emission and is probably due to the removal of a layer of highly polarized gas molecules from the surface.

The close similarity between the values obtained for 918 and for 921 indicates that there is no free aluminum on the surface of the Al_2O_3 promoted catalyst, and also that Al_2O_3 (possibly $FeAl_2O_4$), if it exists at the surface at all, is present in very small quantities.

Catalysts 920 and 922 offer a marked contrast to 918 and 921 in two respects: they possess pronounced temperature coefficients (Fig. 3); and the threshold curves, rather than having the usual sharp feet, skirt the wave length axis for a long distance (Curves 4 and 5, Fig. 2).

The increase in emissivity with rising temperature places these catalysts in the same general class with oxide coated filament such as barium or strontium oxide on platinum. While this peculiar temperature effect has been observed on oxide filaments by many investigators, its cause is still a matter of conjecture. Case[11] feels that in heating the oxide the pure metal is to some extent set free, thus increasing the threshold since the long wave length limit is much higher for the pure metals than for the oxides. Becker[12] has obtained excellent evidence to support his contention that the activity of oxide coated filaments is due to metallic barium on the surface of the barium oxide. Crew,[13] on the other hand, feels that during the heating process a thin film of the base metal of the filament becomes built up over the surface and that the work function of this film decreases with temperature. The characteristics of the threshold curves in Fig. 2 should throw much light on this question.

The distinctive shape of Curves 4 and 5 in Fig. 2 for the long wave

[11] Case, Phys. Rev., 17, 398 (1921).

[12] Becker, *ibid.*, 34, 1323 (1929).

[13] Crew, ibid., 28, 1265 (1926).

length limit shows unquestionably that the photo electrons arc emitted from a composite surfacr similar in nature to that described where potassium was electrolyzed into platinum.[5] The long wave length limit for iron is very close to 2575 Å., while that for pure potassium is 5600 Å. in layers of one or more molecules deep. The thresholds for K_2O and $K_2Al_2O_4$ are unknown, but they must be at least as low, probably lower, than for pure iron, since the presence of oxvgen, even in traces, drops the long wave length limit to that given by line 2, Fig. 2, for pure iron.

The threshold for 920 at 400° is about 4450 Å., while for 922 under the same conditions it is about 3330 Å. Not only are both of these values far below that for pure potassium, but the current intensity was comparatively low for λ3130, which line is near the maximum wave length sensitivity for potassium.

The conclusion to be drawn from the above consideration is, therefore, that the composite emitting surface in both cases is one of potassium and iron, and that the quantity of free potassium on the surface is small, far less than a monomolecular layer. It will be noted that the ratio of free potassium to iron in 922 is small compared to 920, in spite of the fact that the total potassium contents have the ratio of 26 to 20.

These observations substantiate the contentions of Case and of Vecker that the activity of the oxide is due to a small amount of the metal which has become reduced.

The increase in photoelectric emissivity with rising temperature can only come from an increase in the amount of free potassium on the surface. In Fig. 3 Curves 1 and 2 show an increased emissivity with temperature to about 350" followed by a minimum near 450" with an increase thereafter up to about 700". The minimum is only faintly evident for descending temperatures or for constant temperatures. The most probable explanation of these results is that the increase up to 350° is due to an increased dissociation of K_2O, yielding free potassium, just as was pointed out by Becker for oxide coated emitters. Above 350° evaporation from the surface decreases the free potassium content and results in the minimum at 450°. Above this temperature the diffusion of potassium through the iron to the surface again caused the emissivity to rise. Since the rates of migratibn and evaporation, as well as the dissociation of K_2O decrease with temperature, Curve 3 of Fig. 3 should not show a pronounced minimum for decreasing temperature.

An idea as to the possible source of the free potassium can be had from the character of the emission curves. Catalyst 920 contains only iron and K_2O, hence the potassium must come from the dissociated oxide. Catalyst 922 is made by reducing a mixture of Fe_3O_4, Al_2O_3 and K_2O, during which process all the K_2O is supposed to combine with the Al_2O_3 to form $K_2Al_2O_4$. The potassium must come, therefore, either from the dissociation of the $K_2Al_2O_4$ or from some K_2O which is left uncombined in the iron. Since the long wave length limit shows that the ratio of elemental potassium to the total potassium content is greatly reduced by the presence of the alumina, either the quantity of uncombined K_2O is small or else the $K_2Al_2O_4$ dissociates at such high temperatures that evaporation prevents the accumulation of any appreciable quantity of potassium in the iron. The fact that 922 fatigues rapidly favors the idea that much of the elemental potassium comes from free K_2O within the iron; the similarity of Curves 1 and 2 to 3 and 4 of Fig. 3 points to a common source. This contention is also substantiated by the fact that although the catalyst readily fatigues to the point where the amount of free potassium is negligible, as shown by the photoelectric emissivity, the positive ion emission occurring at higher temperatures is not greatly reduced.

In Table I it was pointed out that K_2O in itself is a catalytic poison and that only when combined with Al_2O_3 is it an effective promoter. The photoelectric data, however, show that both 920 and 922 possess the same types of heterogeneous surfaces, and that the work functions are quite similar. This apparent conflict is doubtless due to the fact that the photoelectric properties of 922 are determined by the uncombined K_2O while the ability of $K_2Al_2O_4$ to promote catalysis may offset the poisoning action of the remaining small amount of free K_2O.

The mechanism involved in the poisoning action of K_2O is uncertain and is receiving further investigation. It seems probable, however, that it is due to the dissociation of K_2O which takes place at the operating temperature (450°) and that the free potassium and not the oxide is the actual poison.

The writer is especially indebted to Dr. C. H. Kunsman for his criticisms and the constructive interest he has taken in this research; also to Mr. Joseph Reuter, instrument maker, and to Mr. Leonardo Testa, glassblower.

Summary

A study of the photoelectric properties of several types of catalysts used in the synthesis of ammonia has yielded the following results.

The unpromoted iron catalyst made from reduced magnetite has the same photoelectric threshold as electrolytic iron; both show no temperature coefficient over the range investigated. The aluminum oxide promoted iron catalysts also have the photoelectric properties of pure iron. From this it follows that the surface forces for pure iron and reduced magnetite are identical, that no free aluminum collects on the surface of the promoted catalyst, and that the concentration of any aluminum oxide on the surface must be small.

The photoelectric properties of iron catalysts containing K_2O and

$K_2Al_2O_4$ are very different from those of pure iron. The emissivity increases markedly with temperature as is the case for oxide coated filaments, indicating dissociation of the potassium oxide at elevated temperatures. The long wave length limit lies intermediate between that of iron and that of potassium, showing the surface to be sparsely covered with elemental potassium. The long wave length limits show clearly that the ratio of elemental potassium to the total potassium content is greatly reduced by the presence of aluminum oxide.

The photoelectric properties of the $K_2Al_2O_4$ promoted catalyst appear to come from the K_2O which has failed to combine with the Al_2O_3. It is suggested that the poisoning action of K_2O alone is due to the ease with which it dissociates, and that it is the free potassium which is the actual poison.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE SOLUBILITY OF HYDROGEN FLUORIDE IN BENZENE AND IN OCTANE

BY J. H. SIMONS

RECEIVED OCTOBER 17, 1930 PUBLISHED JANUARY 12, 1931

The study of the solubility of gaseous hydrogen fluoride in organic solvents was begun in an attempt to obtain more information about the polymer H_6F_6 whose existence has been indicated by Simons and Hildebrand from considerations of the density of the gas.[1] While the results have not aided greatly in this connection, an example of an unusual type of solution has been found in the case of hydrogen fluoride dissolved in benzene.

Apparatus.—The apparatus, the design of which is shown in Fig. 1, was made entirely of copper with all permanent joints sealed together with silver solder. The three vessels of which the apparatus consisted were held together with screw connections. Two of the vessels were held in separate constant temperature baths; the one served as container for the liquid hydrogen fluoride and the other for the solution. The third vessel, which fastened on the bottom outlet of the solution container, was the constant volume sample tube. Copper is a suitable material for this apparatus, for hydrogen fluoride in the absence of an oxidizing agent, such as oxygen from the air, is without action on it, and oxygen was rigorously excluded.

Materials Used.—The anhydrous hydrogen fluoride was made in the manner described by Simons[2] and distilled directly into the apparatus, which had been carefully cleaned, dried and filled with dry nitrogen. The

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[1] Simons and Hildebrand, THIS JOURNAL, 46, 2183 (1924).

[2] Simons, *ibid.*, 46, 2179 (1924).

benzene was pure thiophene-free material which was fractionated, dried with phosphorus pentoxide and with sodium, and finally distilled directly into the apparatus. The octane was prepared synthetically in this Laboratory and was carefully dried in the same manner as for the benzene. The nitrogen was the commercial gas from a cylinder from which the oxygen was removed by towers of cuprous ammonium chloride solution. It was dried with sulfuric acid and with phosphorus pentoxide.

Method of Procedure.—For the determinations made without the use of nitrogen, the vessel of hydrogen fluoride was allowed to warm up to the boiling point. The gas formed was passed slowly through the solvent, the solvent vessel being kept at a temperature sufficiently high so that liquid hydrogen fluoride would not condense in it. Equilibrium was considered established when samples of the solution taken over intervals of the passage of the gas gave check analyses. Raising the temperature of the solution vessel gave determinations at higher temperatures.

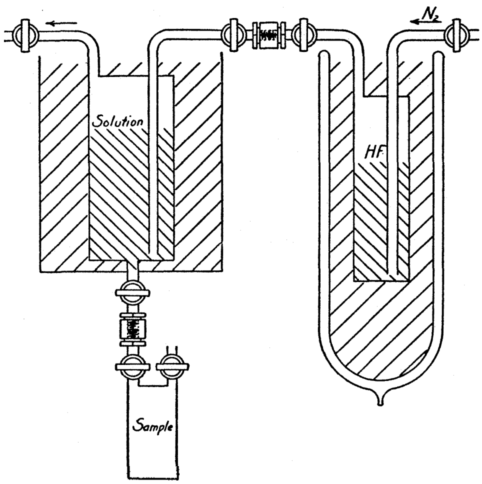

Fig. 1.—Solubility **apparatus.**

For the determinations made with a partial pressure of hydrogen fluoride less than that given by boiling the liquid, nitrogen was passed through the vessel containing it while it was kept at a constant temperature.

The sample for analysis was drawn off into the sample tube, which had a volume of about 20 cc. It was weighed, forced into an aqueous solution containing an excess of sodium hydroxide over that necessary to neutralize the hydrogen fluoride and the excess was titrated with a standard hydrochloric acid solution.

Results

The results of these determinations are recorded in Table I and shown graphically in Fig. 2.

Several different lots of both benzene and hydrogen fluoride were used in these experiments, which extended over a considerable period of time. The agreement of the results indicates that they are free from large accidental errors.

The vapor pressure of hydrogen fluoride from the solution was plotted against its mole fraction at different temperatures as shown in Fig. 3.

It was calculated from the vapor pressure of liquid hydrogen fluoride at the temperature at which the pure liquid was held, the vapor pressure of benzene at the temperature of the solution, and the barometric pressure. Table II shows the data from which the curves were drawn. The mole fractions were taken from the smooth curves in Fig. 2. The straight lines represent the "ideal" vapor pressures of hydrogen fluoride from the solution as calculated from Raoult's law.

It is to he expected that hydrogen fluoride with its high dielectric constant would show a large positive deviation from Raoult's law in benzene solutions. This is found at the higher concentrations but at low concentrations a negative deviation is observed.

TABLE I

SOLUBILITY OF HYDROGEN FLUORIDE IN BENZENE AND IN OCTANE

Solution in benzene								In octane	
Hydrogen fluoride liquid at the boiling point		HF liquid at 0°C.		HF liquid at −18°C.		HF liquid at −77°C.		HF liquid at the boiling point	
Temp. of soln., °C.	Mole fraction HF	Temp. of soln., °C.	Mole fraction HF	Temp. of soln., °C.	Mole fraction HF	Temp. of soln., °C.	Mole fraction HF	Temp. of soln., °C.	Mole fraction HF
23.1	0.0630	25.6	0.0384	23.0	0.0355	23.6	0.0227	25.1	0.00338
31.1	.0525	30.2	.0346	31.8	.0323	30.0	.0208	36.0	.00276
42.3	.0394	40.5	.0277	20.8	.0382	45.0	.0128	45.2	.00235
27.2	.0588	50.0	.0201	31.2	.0306	56.0	.00825	51.0	.00194
33.9	.0495	27.5	.0368	40.8	.0244	65.0	.00557	66.3	.00170
39.1	.0442	52.0	.0181	52.8	.0161	19.6	.0249		
39.4	.0427	56.3	.0150	58.1	.0117	38.3	.0163		
39.2	.0437	65.1	.0084	21.0	.0375	52.9	.0098		
25.8	.0596	21.0	.0425	20.9	.0381	60.8	.0067		
29.3	.0556	32.9	.0330	28.0	.0327				
29.4	.0548	61.2	.0108	38.0	.0258				
32.9	.0507			49.0	.0184				
44.8	.0365			60.6	.0098				
44.7	.0382								
54.1	.0243								
54.1	.0248								
21.5	.0653								
22.0	.0648								
21.6	.0650								
24.2	.0625								
24.2	.0620								
35.6	.0510								
36.7	.0468								
62.5	.0155								
62.4	.0150								
46.0	.0332								
51.0	.0280								
54.0	.0246								
61.0	.0167								
72.8	.00395								

NOTE.—The mole of hydrogen fluoride is taken as the formula weight of the molecular species, HF.

TABLE II

EXPERIMENTAL DATA FOR CURVES

Temp. of soln., °C.	Mole fraction HF in solution Liquid hydrogen fluoride at −77°C.	−18°C.	0°C.	B. p.	Vapor pressure HF	Vapor pressure C_6H_6	Partial pressure of HF over solution, mm. Liquid hydrogen fluoride at −77°C.	−18°C.	0°C.	B. p.
20	0.0248	0.0385	0.0432	0.0673	768	75.6	4.5	147	203	669
30	.0203	.0315	.0355	.0548	1070	120.2	4.2	137	283	625
40	.0158	.0244	.0275	.0422	1470	183.6	3.8	123	254	561
50	.0112	.0173	.0196	.0298	1990	271.4	3.2	104	214	473.6
60	.0071	.0102	.0117	.0180	2630	390.1	2.4	77.5	160	354.9
Vapor pressure HF, mm.	5.1	166	342							
Average barometric pressure, mm.	750	740	742	745						

This is an example of an unusual type of solution. It is similar to the case of pyridine–water[3] in that both positive and negative deviations from Raoult's law are found in the same curve, but it is different in that pyridine has *a* negative deviation at very high concentration, but **a** positive deviation at moderate or low concentrations.

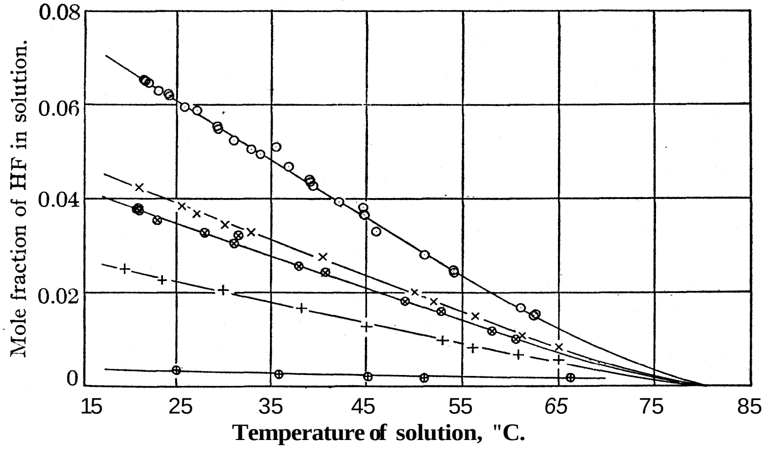

Fig. 2.—Solubility of hydrogen fluoride in benzene and in octane. ○, Solubility in benzene with HF liquid at 19.5°; X, solubility in benzene with HF liquid at 0°; ⊗, solubility in benzene with HF liquid at −18°; +, solubility in benzene with HF liquid at −77°; ⊕, solubility in octane with HF liquid at 19.5°.

A possible explanation of this phenomenon can be given by a consideration of the electric field surrounding the highly polar hydrogen fluoride molecule. When these molecules are in sufficient concentration to exert an

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[3] J. H. Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1924, p. 41.

influence upon one another, they will be mutually attracted and so tend to be removed from the solution. This explains the positive deviation from Raoult's law at high concentration. When the concentration is so low that the distance between the molecules of hydrogen fluoride is great enough to make the mutual attraction small, then the electric field around each of the hydrogen fluoride molecules will attract even the slightly polar benzene molecules and so cause the vapor pressure of hydrogen fluoride from the solution to be less than would be given by Raoult's law.

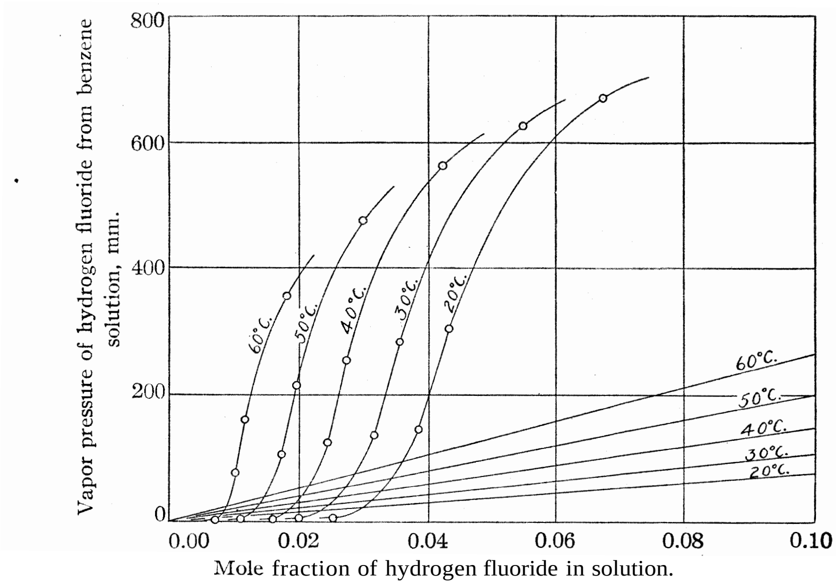

Fig. 3.—Hydrogen fluoride–benzene solution.

The author wishes to acknowledge the assistance of Mr. Eric E. Johnson in making the determinations.

Summary

The solubility of hydrogen fluoride in octane has been measured.

The solubility of hydrogen fluoride in benzene has been measured over a range of temperature and partial pressure of hydrogen fluoride.

The vapor pressure of hydrogen fluoride from a benzene solution shows a negative deviation from Raoult's law at very low concentrations but a high positive deviation at higher concentrations.

A possible explanation of this phenomenon is given.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE SOIL CHEMISTRY LABORATORY, OHIO AGRICULTURAL EXPERIMENT STATION]

DIPHENYLAMINE AS INDICATOR IN THE DETERMINATION OF IRON IN SILICATES

BY C. J. SCHOLLENBERGER

RECEIVED OCTOBER 20, 1930 PUBLISHED JANUARY 12, 1931

Since Knop[1] proposed the use of diphenylamine as internal indicator for titration of ferrous iron with dichromate, a number of investigators[2] have reported their experience with this indicator. Reports in general have been favorable, but it has been noted that the color change is not always sharp, and there is a blank attributed to the volume of oxidizing solution consumed by the indicator itself. The optimum conditions for use of this indicator have not been well defined. Knop stated that the presence of phosphoric acid is advantageous, destroying the yellow color due to ferric salts and so making the end-point more easily seen, but mentions no other advantage from its addition. In the titration of vanadic acid by ferrous sulfate and diphenylamine, Willard and Young[2] specified that the solution should be buffered by addition of sodium acetate sufficient for free hydrochloric and sulfuric acids, and phosphoric acid also added. The intense color of the indicator is developed by the vanadic acid to be determined, and discharged upon complete reduction with ferrous sulfate. They report a considerable blank correction. Sarver[2] states that diphenylamine sometimes gives erratic results in ferrous iron titrations with dichromate, but recommends it for the determination of ferrous oxide dissolved from a mineral by sulfuric or hydrochloric and hydrofluoric acids. The addition of excess boric acid and standard dichromate to minimize oxidation of the iron by air, and deliberate back titration with standard ferrous sulfate, are advised. He further states that it is best to keep the volume of solution small and to take the disappearance of the intense blue as the end-point, disregarding any blue tint which persists; fluoboric acid had no noticeable bad effect, but on the contrary seemed advantageous, brightening the color Diphenylamine has been reported to be a very satisfactory indicator in titration of hydroquinone by ceric sulfate, in presence of either sulfuric or hydrochloric acid and absence of iron.[3]

Recently, the author had occasion to determine ferrous oxide in a mineral, and chose Sarver's procedure for the purpose. The decomposition of the sample having been effected in a 50-ml. platinum crucible, sufficiently

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[1] Knop, THIS JOURNAL, 46, 263 (1924).

[2] Sarver, *ibid.*, 49, 1472 (1927); Schollenberger, *Soil Science*, 24, 65 (1927); Willard and Young, THIS JOURNAL, 50, 1334 (1928); *Ind. Eng. Chem*, 20, 769 (1928); Furman and Wallace, THIS JOURNAL, 52, 1443 (1030); *ibid.*, 52, 2347 (1930); Kolthoff arid Sarver, *ibid.*, 52, 4179 (1930)

[3] Furman, *ibid.*, 50, 1675 (1928).

large to permit titration in the crucible, the additions of boric acid and excess dichromate were omitted, as it was considered that there would be little chance for oxidation in the brief time required for titration. The solution was titrated directly by dichromate in the presence of sulfuric and free hydrofluoric acid. The brilliance and sharpness of appearance of the intense blue end-point color were surprising, entirely at variance with previous experience and Sarver's description of the behavior of the indicator. This suggested that free hydrofluoric acid map have a desirable effect upon the development of the indicator color[4] and some experiments with solutions were undertaken in order to investigate the matter. The conditions chosen for these titrations were such as might prevail in a determination of ferrous oxide in a mineral by a procedure similar to Sarver's, namely, titration in small volume in presence of considerable concentrations of sulfuric or hydrochloric acid. It was also desired to determine whether total iron in the titrated solution could be determined by a titanous chloride–thiocyanate titration after the oxidation of the ferrous iron in the first titration with dichromate and diphenylamine. The behavior of diphenylamine on back titration witn the reducing agent was of interest, so that the determination fitted in the plan for the work. The reduction titration following the oxidation titration would also serve as a check upon the latter and reveal error due to oxidation by air.

Twentieth normal solutions of ferrous ammonium sulfate and potassium dichromate were prepared by dissolving the proper weights of the pure salts in water, previously boiled and cooled, and diluting to volume. The iron solution was stabilized by addition of 1% sulfuric acid to the water. Titanous chloride of approximately the same strength was prepared by diluting the commercial 20% solution (iron-free) with 10% by volume hydrochloric acid, storing and dispensing from a small bore buret with atmosphere of hydrogen over the solution The diphenylamine solution contained 0.5 g. in 50 ml. of concd. sulfuric acid, and two drops were used for each titration in 20–25 ml. initial volume. All reagents were of C. P. analyzed grade, and the same volumetric apparatus was used throughout with precautions to ensure constant delivery usual in careful work. The strengths of the dichromate and iron solutions were checked by permanganate titrations with sodium oxalate as standard, by direct titration of an aliquot of iron solution with dichromate and ferricyanide as external indicator and by electrometric titrations. All these indicated that the solutions were of equal normality, within 0.2%. In titrations with diphenylamine a tint which did not change in two minutes' standing was considered permanent.

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[4] After this paper had been submitted to the editors, the author's attention was called to the fact that Szebellédy, *Z. anal. Chem*. **81,** 97 (1930), had previously observed that in the presence of fluorides the diphenylamine end-point is sharper and more satisfactory.

The results of the first series of titrations with diphenylamine as internal indicator are presented in Table I Titrations 1–6 show that in the presence of hydrochloric or sulfuric acid alone diphenylamine is not a good indicator for titrating a ferrous solution with dichromate. The first blue tint (indicated by a sudden darkening of the yellow-green in the hydrochloric acid solutions) precedes complete oxidation of the iron. Taking the appearance of a permanent brilliant blue as the end-point, the indications are apparently quite good in hydrochloric acid, but still low in sulfuric acid solution. Increasing quantities of the latter make the results worse. Upon back titration with titanous chloride, the color fades in reverse order. The thiocyanate end-point in this titration is very sharp, but the results are evidently affected by the volume of dichromate required, hence depend upon the characteristics of diphenylamine in the first titration.

The addition of one-tenth the final volume of 85% phosphoric acid results in sharpening the diphenylamine end-point in a remarkable manner, reducing the volume of dichromate required to take the color from the first permanent blue tint to the brilliant blue end-point color to only about 0.02 ml. The disappearance of the color on back titration is not quite so sharp, but still very satisfactory. The thiocyanate end-point in presence of phosphoric acid was poor, the color for some time prior to the end-point being a faint yellow instead of deep yellow with a pronounced red tinge up to the last drop, as is normal. In the dichrornate titration the phosphoric acid entirely destroyed the yellow due to the ferric ion and so made the appearance of the diphenylamine blue very distinct. However, it is plain that this is not the sole explanation for its good effect, as in the absence of phosphoric acid good results were obtained in the intensely yellow hydrochloric acid solutions (Titrations 1–3), while in sulfuric acid solutions (Titrations 4–6) the yellow color was much less, but the titrations less accurate. In Titration 12 the addition of **3** ml. of phosphoric acid was sufficient to destroy the yellow color, yet the results were low and were improved by a further addition of phosphoric acid. Apparently twice as much of phosphoric as of sulfuric acid is necessary for accurate results. The addition of phosphoric acid results in a greater volume of dichromate being required to develop the diphenylamine color, and this excess of oxidant causes an increase in the volume of titanous solution required to reduce the iron again, so that this does not appear to be due to the presence of an oxidizable impurity. The extra amount of phosphoric acid used in this titration did not make the thiocyanate end-point noticeably worse than with the smaller volume.

In Titrations 13–18 twice the volume of hydrofluoric acid (48%) was substituted for the phosphoric acid. The effect in sharpening the diphenylamine end-point is even more marked; the intense end-point color is permanent after the addition of only 0.01 ml. of dichromate beyond that necessary to produce a faint tinge of blue, but is discharged with equal sharpness on back titration. The thiooyanate end-point in solutions containing free hydrofluoric acid is greatly in error, however, as the color is never intensely red, quickly becomes yellow as the reduction proceeds and even this disappears before all iron is reduced. The addition of boric acid in excess tics up all hydrofluoric acid as fluoboric acid, restores the yellow color of ferric iron or the intense blue of diphenylamine if present and just faded in hack titration, and permits a very satisfactory end-point with thiocyanate. With all proportions of hydrochloric acid tried, the diphenylamine end-point in presence of free hydrofluoric acid was equally sharp, but the total volume of dichromate required to develop the color increased with proportion of hydrochloric acid.

In solutions containing sulfuric and hydrofluoric acids the diphenylamine end-point was Sully as satisfactory in development, but did not disappear quite so sharply on back titration. After addition of boric acid, the thiocyanate end-point was equally good, and the results of both titrations indicate that the relative proportions of hydrofluoric and sulfuric acids are of no importance (Titrations 16–18). However, other experiments to test the effect of dilution, in one keeping the concentration of sulfuric acid constant, indicated that the total volume of sulfuric acid present should not exceed that of hydrofluoric acid. Otherwise, the degree of dilution apparently made little difference, although not without practical importance since the color change is slow at high dilutions (Titrations 30–31)

In the presence of fluoboric acid with either sulfuric or hydrochloric acid (Titrations 19–24), the diphenylamine end-point was invariably premature in appearance and lacked sharpness The behavior was similar to that of a solution containing sulfuric acid alone, and the bad effect of excessive concentration of the latter was increased. The only differences noted were an increase in the intensity of the color at corresponding stages of the titration, as noted by Sarver, and slightly more rapid color changes. Unlike phosphoric and hydrofluoric acids, fluoboric acid does not reduce the yellow color due to ferric ions, and has no bad effect upon the thiocyanate end-point.

The titration curves shown in Fig. 1 were drawn from potentiometric data, using a saturated potassium chloride-calomel electrode at approximately 25°. The volume of solution at the beginning was 20–25 ml. as in the titrations in Table I, contained in a 100-ml. beaker with rod for stirring. The color of the indicator was observed in these titrations, and its appearance noted on the curves as follows: first faint tinge permanent for one minute, an open circle; pronounced color about half that of the brilliant end-point, a circle with central dot; the usual brilliant end-point tint, a cross; maximum color developed by excess dichromate, an inked-in circle.

TABLE I

TITRATION OF IRON

In solution containing 10 ml. of N 0 050 $Fe(NH_4)_2(SO_4)_2$ with concentrated acid specified and 2 drops of diphenylamine solution diluted to 20–25 ml. with water by N 0 050 $K_2Cr_2O_7$. The oxidized iron then titrated with *N* 0 044 $TiCl_3$ and 0 5 g of KCNS

Titration	Concd acid etc , added, ml.		Standard $K_2Cr_2O_7$ required Permanent blue tint, ml	Brilliant end point, ml	Standard $TiCl_3$ required To fade all blue, ml.	To fade thiocyanate color, ml
1	HCl	1 5	9 62	9 97	0 38	11 30
2	HCl	3 0	9 50	10 00	.50	11 34
3	HCl	6.0	9 75	10 02	20	11 30
4	H_2SO_4	1 5	9 40	9 95	.00	11 30
5	H_2SO_4	3 0	9 60	9 85	.42	11 15
6	H_2SO_4	0 0	8 0	8 9	1 0	10 12
	H_3PO_4	3 0 with				
7	HCl	1 5	10 02	10 04	0 03	11 35
8	HCl	3 0	10 03	10 05	03	11 37
9	HCl	6 0	10 03	10 06	.05	11 40
	H_3PO_4	3 0 with				
10	H_2SO_4	1 5	10 05	10 07	03	11 44
11	H_2SO_4	3 0	10 04	10 05	03	11 42
12		6 0	9 85	9 87		
	Added H_3PO_4	5 0	10 01	10 03	02	11 45
	HF	6.0 with				
13	HCl	1.5	9 96	9 97	01	11 37[a]
14	HCl	3 0	10 04	10 05	01	11 30"
15	HCl	6 0	10 11	10 12	01	11 29[a]
	HF	6 0 with				
16	H_2SO_4	1 6	10 05	10 06	02	11 30[a]
17	H_2SO_4	3 0	10 05	10 06	01	11 28"
18	H_2SO_4	6 0	10 05	10 06	02	11 28"
	HF 6, H_3BO_3 4 g					
19	HCl	1 5	9 88	10 01	30	11 26
20	HCl	3 0	9 48	9 93	35	11 18
21	HCl	6 0	9 58	10 00	40	11 23
	HF 6, H_3BO_3 4 g					
22	H_2SO_4	1 5	9 85	9 98	35	11 25
23		3 0	9 73	9 93	32	11 20
24	H_2SO_4	6 0	6 1	7 3	.75	8 3
	HF 6, H_2SO_4 3					
25	20 ml Fe soln		20 01	20 02	01	22 60[a]
26	10 ml Fe soln		10 04	10 05	01	11 28[a]
27	pyrex beaker		10 05	10 06	.02	11 29"
28	Same, titrated		10 03	10 04	.02	11 31[a]
29	in platinum		10.01	10 02	01	11 31"
	HF 6, H_2SO_4 6					
30	Diluted to 200 ml.		10.09	10.10	.01	11 30"
	HF 6, H_2SO_4 20					

TABLE I (*Concluded*)

Titration	Concd. *acid, etc., added,* ml.	*Standard* $K_2Cr_2O_7$ required		Standard $TiCl_3$ required	
		Permanent blue tint, *ml.*	*Brilliant end-point,* ml.	To fade all blue, ml.	To *fade* thio cyanate color, ml.
31	Diluted to 200 ml.	10.03	10.05	..	...
	Added HF 12	10 07	10 08	0 02	11 28[a]

[a] Four *g.* of powdered boric acid worked to a smooth paste with a little water added previous to titration with titanous chloride. Titration 31 had 10 g. of boric acid.

Curve I shows the effect of excessive concentration of sulfuric acid, about one-fourth the volume at the end of the titration. The e. m. f. readings are highest, and the maximum indicator color was developed prior to complete oxidation of iron.

Curve II shows the effect of fluoboric acid from 6 ml. of hydrofluoric acid, in the presence of 3 ml. of sulfuric acid in a final volume of approximately 30 ml. During the first part of its course this curve follows the first closely. The maximum color was developed just a little short of complete oxidation of iron.

Curve III indicates the effect of a moderate concentration of sulfuric acid, one-tenth the final volume The development of color is premature, but the standard end-point color is reached at about the true end-point, as indicated by the titration curve.

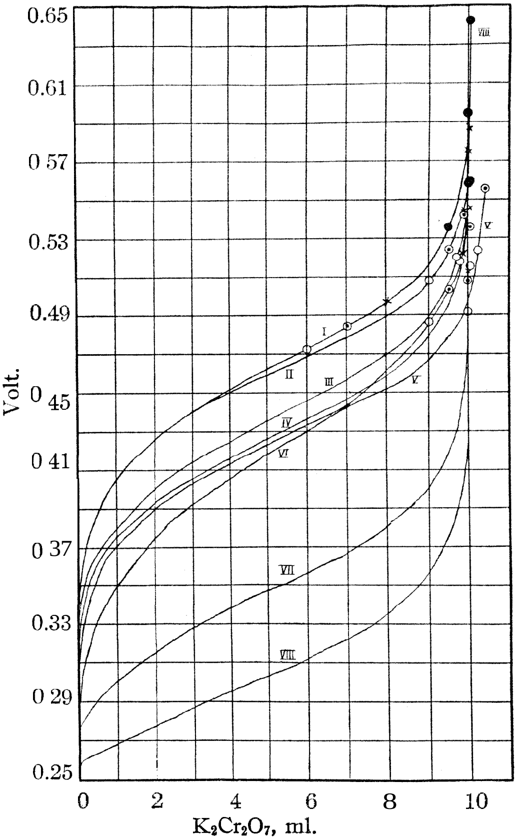

Fig. 1.—Electrometric titration of 10 ml. of 0.05 *N* ferrous ammonium sulfate with various additions by 0.05 *N* dichromate.

Curve IV was intended to show the effect of the sulfate ion in a solution saturated with potassium sulfate upon the activitv of sulfuric acid in one-tenth final volume. The common ion had a noticeable effect upon the e. m. f. without resulting in any important change in the position of the color or electrometric end-points.

Curve V shows the effect of buffering with 5 g. of potassium acetate a solution containing 3 ml. of sulfuric acid in 30 ml. final volume. The effect upon both color and potentiometric end-points is bad, neither being developed by a considerable excess of dichromate. Willard and Young[2] recommended reduction of the effective acidity by addition of acetate and phosphoric acid only in the titration of an oxidizing agent by ferrous sulfate, and not in titration of ferrous salt by an oxidizing reagent.

Curve VI was determined in presence of one-fourth final volume of hydrochloric acid. The intense yellow interfered with observation of the diphenylamine end-point, but it could be seen that it was premature. The electrometric end-point was sharp and accurate.

Curve VII indicates the effect of one-tenth final volume each of sulfuric and 85% phosphoric acids. Phosphoric acid has a very pronounced effect in lowering the oxidation potential, and the standard end-point color is developed at the flex-point of the titration curve. All of the color changes are in the steep portion of the curve, explaining the sharpness of the indicator under these conditions.

Curve VIII shows that one-fifth volume hydrofluoric acid and one-tenth volume sulfuric acid has the optimum effect upon the sharpness of the color end-point with diphenylamine. The first portion of the curve is quite flat, indicating that hydrofluoric acid largely overcomes the oxidation–reduction buffer effect in iron solutions. The asymptotic portion of the curve begins with a sharp bend and is nearly vertical, so that a very small addition of dichromate results in a great increase in potential. The first appearance of color is apparently near the true flex-point of the curve, and other changes are well separated on the e. m. f. scale but produced by very small increments of oxidizing agent, explaining the apparent sensitivity of the indicator in this titration.

With the exception of Curve V, PH buffered by acetate, Curve VIII, determined in presence of free hydrofluoric acid, shows the greatest requirement of dichromate to develop color, *i. e.*, the highest blank. The explanation for this is that the depression in oxidation potential produced by the fluoride ion requires an appreciable addition of dichromate to raise it to the point at which the color appears. As shown very recently by Kolthoff and Sarver,[2] the product of the partial oxidation of diphenylamine is a true oxidation–reduction indicator, developing color at a definite oxidation potential. The experiments herein reported indicate that the development of color is affected by other factors also, e. g., concentration of sulfuric acid. Under the conditions of a practical titration, the color change is perfectly reversible, as shown by such changes and e. m. f. readings on back titration with titanous chloride corresponding with those in the first titration. While Kolthoff and Sarver have shown that there is a certain consumption of oxidizing agent required for development of color, it is evident that a part of the apparent blank noticed in titrations is simply the volume of dichromate necessary to raise the oxidation potential of the solution to the point at which the color appears.

The influence of phosphoric and hydrofluoric acids upon the diphenylamine end-point in iron titrations is due to inactivation of the ferric ion in compounds less ionized than the sulfate, chloride or fluoborate, and the same explanation also applies to the effect upon the thiocyanate end-point. Inactivation of the ferric ion is desirable in the oxidation titration, as it diminishes the buffer effect upon oxidation potential normal to mixtures containing both ferrous and ferric ions. It is undesirable in the reduction titration because ferric fluoride is evidently less dissociated than the thiocyanate, so that the colored compound is not formed.

The practical conclusion to be drawn from the foregoing is that the presence of hydrofluoric acid is advantageous in a titration of ferrous iron with diphenylamine as indicator. Addition of boric acid to inactivate the hydrofluoric acid employed in decomposition of a silicate for ferrous iron determination should be omitted. The reasons for this addition, first recommended by Barnebey,[5] are not of importance if a proper procedure is followed. In the first place, the danger of oxidation by air of ferrous iron in the presence of free hydrofluoric acid has been overemphasized. As Hillebrand and Lundell[6] state, if the solution is cooled before air comes in contact with it and the titration is completed without delay, there is no appreciable error from oxidation by exposure to air. Practically all chance of this can be avoided by titrating in the crucible in which the decomposition was effected. That this is practical is shown by the results obtained in Titrations 28 and 29 in Table I. In the second place, manganese, which is oxidized to the trivalent state by permanganate in the presence of free hydrofluoric acid, does not in the least interfere in a dichromate–diphenylamine titration. This was shown by titrating a solution containing 0.5 g. of manganous sulfate, 3 ml. of sulfuric and 6 ml. of hydrofluoric acids and 10 ml. of iron solution. A large excess of permanganate added to a similar mixture produced no permanganate color, but on addition of diphenylamine the intense color of the latter was developed instantly and required very nearly the theoretical volume of titanous chloride to discharge. Diphenylamine also gave correct indications in a similar direct titration with permanganate.

A further conclusion is that titration by standard titanous chloride solution with thiocyanate as indicator is a practical method for determination of total iron in the case of silicates completely decomposed by hydrofluoric and sulfuric acid treatment. It is only necessary to add excess boric

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[5] Barnebey, THIS JOURNAL, **37, 1481** (1015).

[6] Hillebrand and Lundell, "Applied Inorganic Analysis." John Wiley and Sons, Inc., New York. 1929, **p.** 775.

acid to the solution just titrated for ferrous iron, as fluoboric acid is harmless, while hydrofluoric acid is very detrimental to either the thiocyanate or methylene blue end-points. The two titrations fit well together; both are at their best when the volume of solution is small and the sulfuric acid concentration is high, about one-tenth final volume being near the optimum. Both titrations show very sharp and distinct color changes at the end-point, so that it is practical to titrate in the platinum crucible in which the sample was decomposed. The observation that hydrofluoric acid lowers the oxidation potential of ferric solutions indicates that decomposition in platinum is probably safer than might be inferred from the known fact that ferric chloride is reduced to some extent by long contact with platinum.

Sarver[2] described a transparent cover of bakelite for a platinum crucible to be used in decomposing the sample of mineral for ferrous iron determination. He neglected, however, to publish a cut of his apparatus, nor was it described in much detail. The author had one made[7] which has given good results in use. It is shown in Fig. 2. The taper is polished, and makes an almost gas-tight joint with the edge of the crucible. It is provided with a tube of bakelite for leading in carbon dioxide from a Kipp generator, and a stoppered opening for adding reagents, stirring, etc. In use the procedure has been as follows: the ground sample is weighed and transferred to the 50-ml. crucible for which the cover was made. The latter is firmly placed, and the crucible set in a hole in asbestos board over a micro burner. By means of a short rubber tube a small bubble counter attached to the source of carbon dioxide is connected to the bakelite tube and the gas allowed to flow for a sufficient time, to expel air from the crucible. About 6 ml. of boiled and cooled water is added, followed by the careful addition of 6 ml. of 1:1 sulfuric acid. This mixture is heated to boiling, while the flow of gas continues. The stopper is removed and 6 ml. of hydrofluoric acid poured in from a small crucible in which it may be measured with sufficient accuracy. By moving the asbestos board the acid in the crucible may be stirred, so that undissolved particles are more easily visible. The gas pressure is kept on all the while and the crucible heated carefully, but the acid need not be boiled vigorously. As the stopper is in place during this time, no air can enter and but little carbon dioxide is used. When decomposition is complete, heating is discontinued and the crucible allowed to cool. When it can be handled without discomfort, it may be lifted from the asbestos board and set in a dish of water to cool more rapidly. When quite cold the stopper is removed and sufficient water added to dilute the solution to about 25 ml. Two drops of diphenylamine solution are added, and the dichromate added carefully, stirring with a platinum spatula. As soon as a drop of the dichromate produces a permanent blue color, the iron is entirely oxidized and the titration of ferrous iron finished. If total iron is to be determined, 4 g. of boric acid rubbed to a smooth paste with a little water, to avoid lumps, is added and stirred until dissolved. This is likely to intensify the blue color of diphenylamine, but it is of no

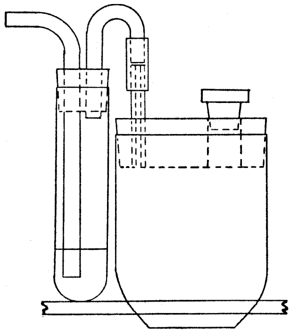

Fig. 2.—Platinum crucible with bakelite cover in place and trap attached.

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[7] By the Apex Specialties Corp., 1184 Flushing Ave., Brooklyn, N. Y.

consequence as it will disappear later. Five ml. of 10% potassium thiocyanate solution is added, followed by standard titanous chloride until all red has disappeared, and any remaining yellow ceases to diminish with another fractional drop of the solution. If the crucible becomes too full during the course of titration, it is placed in a beaker and upset, the titration being continued without removing the crucible. Even if the solution contains free hydrofluoric acid, the amount of iron dissolved from a pyrex beaker in a short time will cause no appreciable error. After addition of boric acid, the glass is not attacked at all.

Bakelite is not an ideal material for the crucible cover, being somewhat attacked by the hot acid vapors, and evidently decomposed at the surface to some extent, as a pronounced phenolic odor was noted in the solution obtained the first time the cover was used, and poor results were obtained in this titration. After use a half dozen times the odor was no longer noticeable, the behavior on titration was normal and the blank determination indicated that only 0.02 ml. each of 0.05 N dichromate and titanous chloride were necessary for good end-points. By this time the surface of the cover had been attacked to such an extent that it was no longer transparent, so that the stopper had to be removed when it was desired to observe the progress of solution. Escape of gas during the time the stopper is removed is sufficient to prevent entrance of air, and there need be no error from oxidation.

Sarver[2] has stated that the chief reason for the use of dichromate rather than permanganate for titration of ferrous iron dissolved from a sample of mineral is the decreased tendency to oxidation of organic matter by dichromate, so that the latter would be expected to furnish more accurate results in its presence. The author has made a few experiments to determine whether organic matter has an appreciable effect upon the dichromate–diphenylamine titration in presence of sulfuric and hydrofluoric acids. Ammonium oxalate equivalent to 14 ml. of 0.05 N solution was added to a mixture of 10 ml. of 0.05 M ferric sulfate, 6 ml. hydrofluoric and 3 ml. of sulfuric acids, total volume, 20 ml. This was boiled for fifteen minutes in a platinum crucible, simulating the conditions of an actual determination of ferrous oxide in a mineral. Upon titration, 0.02 ml. of dichromate produced a permanent diphenylamine end-point and the usual amount of titanous chloride solution was consumed in reducing the iron, indicating no reduction of ferric salt by the oxalate, and that the latter does not by itself consume dichromate during the titration. However, in similar experiments in which an aliquot of ferrous solution also was added, from 10 to 25% excess dichromate was required to produce the diphenylamine end-point, but in the back titration with titanous chloride only the amount corresponding to the total iron content was consumed. These results indicate that organic matter, at least oxalic acid, can cause high results for ferrous iron, but only in proportion to the amount of the latter present. Numerous examples of similar reactions are known, in which a substance is not normally oxidized by dichromate, but is oxidized to a certain extent when accompanied by an easily oxidized substance. This has been explained as being due to intermediate formation of Cr^{V} which has higher oxidizing potential than Cr^{VI}.[8] The brightening of the diphenylamine color noted when a trace of ferrous salt is added to a slightly overrun titration with dichromate is possibly another instance, but the presence of ferrous iron is not essential to formation of color.

Summary

The properties of diphenylamine as indicator in dichromate titration of a solution containing ferrous iron, hydrofluoric and sulfuric or hydrochloric acids, as obtained in the determination of ferrous oxide in a silicate, have

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[8] Lang and Kurtz, Z. *anorg. allgem. Chem.*, *181, 111 (1929).*

been investigated. In presence of sufficient hydrofluoric acid in proportion to sulfuric or hydrochloric acid, diphenylamine is an excellent indicator for this titration. The presence of diphenylamine does not prevent an accurate determination of the total iron in the solution by a reduction titration with titanous chloride and thiocyanate indicator, following the oxidation titration, provided the hydrofluoric acid necessary in the first titration is inactivated by addition of excess boric acid prior to the second.

Potentiometric titration curves show that the pronounced effect of hydrofluoric (also phosphoric) acid in increasing the sharpness of the diphenylamine end-point in iron titrations is due to a lowering of the oxidation potential in a solution containing both ferrous and ferric ions, which is high enough under the usual conditions of the titration to cause the indicator color to develop prior to complete oxidation of the iron. The effect of these reagents upon the thiocyanate end-point in the reduction titration and upon the color of solutions containing ferric salts indicates that the underlying cause is the slight dissociation of ferric fluoride (or phosphate).

Based upon these observations, an improved procedure for the determination of ferrous and ferric oxides in silicates is described. Manganese does not interfere in the dichromate titration with diphenylamine in the presence of hydrofluoric acid, but it is shown that in the presence of organic matter results for ferrous oxide may be expected to be high in proportion to the amount of ferrous oxide actually present.

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THE REDUCTION POTENTIAL OF THE CERIC–CEROUS ELECTRODE

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RECEIVED NOVEMBER 6, 1930 PUBLISHED JANUARY 12, 1931

Introduction

The only work upon the reduction potential of the ceric–cerous electrode recorded in the literature is the early research of Bauer and Glaessner,[2] which involved several factors that diminished its accuracy and reliability. Thus the measurements were made at room temperature, no statement being made about its constancy, and a saturated solution of potassium chloride was used to eliminate liquid potentials. In view of these imperfections and of the recent interest in the use of ceric sulfate solutions for analytical work,[3,4] it seemed advisable to make a thorough study of the

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[1] National Research Fellow in Chemistry.

[2] Bauer and Glaessner, *Z. Elektrochem.*, 9, 534 (1903).

[3] Willard and Young, THIS JOURNAL, 50, 1322 (1928), *et seq.*

[4] Furman, *ibid.*, 50, 755 (1928), *et seq.*

ceric–cerous potential under a wider range of carefully controlled conditions.

The cell studied may be represented as follows

Pt + H_2, H_2SO_4 (0.5 or 1.0 f), H_2SO_4 (0.5 or 1.0 *f*) + $Ce_2(SO_4)_3$ (c_1) + $Ce(SO_4)_2$ (c_2), Pt

There are in this cell three sources of potential: the potential of the hydrogen electrode against sulfuric acid, the potential of the ceric–cerous electrode, and the liquid potential. By making the concentration of the sulfuric acid in both half-cells the same and making the concentration of the sulfates of cerium small, the liquid potential was made negligible.

The author wishes to express appreciation for the suggestions and interest of Professor A. A. Noyes during the progress of the research and for his assistance in preparing this paper for publication.

Apparatus and Materials

The apparatus was essentially that used by Popoff and Kunz[5] in studying the ferric–ferrous electrode. An all-glass electrode vessel was used as before, but the chambers were made smaller to facilitate a more rapid saturation of the acid with hydrogen in the hydrogen half-cell. Instead of a rotary stirrer in the cerium half-cell, the solution was stirred by blowing in an inert gas.

The cell was placed in a thermostat at 25.00° maintained constant within 0.01°. A Leeds and Northrup Type K potentiometer was used.

The hydrogen for the hydrogen electrode was generated by electrolyzing a 5% solution of sodium hydroxide between a nickel and a platinum electrode. The gas was passed through a purifying train and a saturator before entering the cell.

All chemicals with the exception of the cerium salts were of the best grade obtainable and were used without further purification. The water had been redistilled.

The cerium salt was prepared from a commercial cerium oxalate. An analysis by the bismuthate method of Metzger[6] of the ignited oxides obtained from this material showed them to contain less than 48% CeO_2. Assuming that all other rare earths and thorium, iron and calcium might be present, a number of methods were used in attempts to prepare the pure ceric oxide needed.

The best results were obtained by the basic ceric nitrate–bromate process.[7] The crude oxalate was partially ignited to CeO_2, and the residue was moistened with water and treated with nitric acid. The undecomposed oxalate helps reduce the ceric oxide to cerous nitrate. Oxalic acid was added until most of the material was reduced, and the reduction was completed with hydrogen peroxide.

After filtration and evaporation to small bulk to eliminate the large excess of nitric acid, the solution was diluted, potassium bromate was added, and the mixture was boiled until fumes of bromine were evolved. Marble was then added in large pieces, and the boiling was continued with the occasional addition of a little nitric acid. Even with this precaution the precipitate was not free from other rare earths. In the later attempts the basic salt was filtered off and digested for thirty minutes with very dilute nitric acid. Two applications of the entire process were required to produce an oxide which, when converted to the sulfate, would dissolve completely in water.

The purified basic salt was dissolved by nitric acid and oxalic acid and the solution

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[5] Popoff and Kunz, THIS JOURNAL, 51, **382** (1929).

[6] Metzger, *ibid.*, **31,** 523 (1909).

[7] James and Pratt, *ibid.*, **33,** 1326 (1911).

filtered. Cerous oxalate was then precipitated and thorium was removed by digesting the precipitate with ammonium oxalate solution. The oxide prepared by ignition of this oxalate was very pale yellow.

A weighed portion of the oxide was heated to fuming with sulfuric acid for an hour. The sulfate went into solution in water slowly, but completely. An analysis of this solution made by titration with standard ferrous sulfate after oxidation with persulfate with silver ion as a catalyst as recommended by Willard and Young[8] showed the product to contain 99.89% of cerium dioxide. This is within the limits of the experimental precision obtained in the analyses.

Preparation of Solutions.—A large quantity of the purified ceric oxide was converted to the sulfate by heating it with concentrated sulfuric acid. The solution was diluted to a volume in which the total cerium content was about 0.07 formal and the sulfuric acid about 0.75 formal. The total cerium content per gram of solution was then determined by standard ferrous sulfate after oxidation by persulfate. Similarly, the ceric content was determined by direct titration with standard ferrous sulfate. All titrations were made electrometrically. The close agreement observed between the ceric and the total cerium concentrations indicated that there is very little auto-reduction of the ceric sulfate solutions. Analyses of ceric sulfate solutions in sulfuric acid concentrations used in this study over a period of several months bear out the observations of Willard and Young and of Furman that ceric sulfate solutions are remarkably stable. The total sulfate concentration per gram of solution was then determined gravimetrically after dilution by weight. From these values the amount of water (or of more concentrated sulfuric acid) required to make the formality of the sulfuric acid exactly 0.5 (or any other value) was calculated.

Cerous sulfate solution was prepared by reducing ceric sulfate solution with hydrogen peroxide, crystallizing out the salt by concentration, and washing it free from peroxide. This salt was then dissolved in sulfuric acid, and the solution was diluted to the extent required.

The Electromotive Forces and Electrode Potentials.—The electromotive force E of the cells can be expressed as follows

$$E = E_0 - 0.0591 \log \frac{P_{H} (\mathrm{Ce}^{IV})\ \alpha^{IV}}{a_{H^+}(\mathrm{Ce}^{III})\ \alpha^{III}}$$

The data are given in Table I. Here the "observed" electromotive force represents the electromotive force of the cells as measured at 25°, and the "corrected" electromotive force represents this value corrected to a hydrogen pressure of one atmosphere and to a value of the ratio $(\mathrm{Ce}^{IV})/(\mathrm{Ce}^{III})$ equal to unity. The only other variable within any series of experiments in which the acid concentration is constant should then be the activation ratio α^{IV}/α^{III}; and except in so far as this ratio varies there should be no difference between the values of the corrected electromotive forces of the different cells.

Table I shows that, so long as the sulfuric acid concentration is constant, the electromotive force is changed only slightly (at most by 0.7 mv.) either by varying the total concentration of the two cerium salts (even 15-fold) or by varying the ratio of the concentrations of the ceric and cerous salts (even 13-fold). This shows that the activities of the ceric and cerous

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[8] Willard and Young, THIS JOURNAL, 50, 1379 (1928).

TABLE I

ELECTROMOTIVE FORCES AT 25° OF CELLS

$$, \left\{H_2SO_4 \begin{matrix}0.5 \text{ or}\\ 1.0f\end{matrix}\right\}, \left\{\begin{matrix}Ce^{IV}\\ Ce^{III}\end{matrix} + H_2SO_4 \begin{matrix}0.5 \text{ or}\\ 1.0f\end{matrix}\right\}, Pt$$

Series no.	Cell no.	H_2SO_4, f	$(Ce^{IV})^a + (Ce^{III})$	$(Ce^{IV})/(Ce^{III})$	Electromotive force Observed	Electromotive force Corrected
1	1	0.5	20.74	1 000	1 4610	1.4617
	2		11.638		1.4602	1.4609
	3		9.472		1 4600	1.4607
	4		8 832		1.4600	1.4607
	5		6 234		1.4600	1.4607
	6		6 094		1 4000	1.4607
	7		ti 072		1 4601	1.4608
	8		4 736		1.4598	1.4605
	9		3 778		1 4598	1.4605
	10		3 044		1 4597	1.4604
	11		1 384		1 4596	1.4603
II	1	0.5	4 000	0.1351	1.4088	1.4610
	2			0.5248.	1.4436	1.4609
	3			1.260	1.4659	1.4607
	4			3.503	1.4923	1.4608
	5			11.16	1.5221	1.4608
	6			18.16	1.5351	1.4609
III	1	1 0	15.808	1.000	1 4430	1.4437
	2		15.456		1.4431	1.4438
	3		8.450		1.4428	1.4435
	4		4.802		1.4428	1.4435
	5		2.832		1.4428	1.4435
	6		1.162		1.4426	1.4433
	7		1.988		1.4426	1.4433
IV	1	1.0	4.000	10.903	1.5042	1.4435
	2			2.041	1.4612	1.4436
	3			0.3336	1.4145	1.4434
	4			.1402	1.3921	1.4433

[a] Concentration expressed in millimoles per 1000 g. of solution.

ions Ce^{4+} and Ce^{3+} are always proportional to the concentrations of the respective salts. This result doubtless arises from the fact that sulfuric acid and sulfate ion are present at a substantially constant concentration very much greater than that of the cerium salt.

Inasmuch as the total molal concentration of the cerium salts is at most only 2% of that of the hydrogen ion of the sulfuric acid, the liquid potential must be so small as to be negligible, and the corrected electromotive forces (with sign reversed), namely, the values −1.461 and −1.443, represent almost exactly the electrode potential of the cerous–ceric combinations in the presence of 0.5 *f* and of 1 f sulfuric acid, respectively, referred to the electrode potential (taken as zero) of hydrogen against these two concentrations of acids, respectively.

Since there seem to exist no electromotive force measurements which enable the electrode potential of hydrogen against 0.5 and 1.0f sulfuric acid to be referred to the usual standard of electrode potentials, that of H_2 (1 atm.), H^+ (1 m) taken as zero, the ceric–cerous potentials cannot at present be expressed accurately with reference to this standard. However, the activity of hydrogen ion in 1.0 f sulfuric acid is probably not greatly different from 1 molal in view of the facts that its concentration (owing to the probably complete ionization of the acid into H^+ and HSO_4^- and its relatively small ionization, perhaps 5 to 10%, into $2H^+ + SO_4^=$) is somewhat greater than 1 molal and its activity coefficient is somewhat less than unity (0.823 if like that of 1 *m* HCl). The value -1.44 volts therefore represents (almost certainly within 0.01 volt) the molal reduction potential of ceric and cerous sulfate in 1.0 formal sulfuric acid.

Summary

In this article have been described measurements at 25° of the electromotive force of cells consisting of a hydrogen gas electrode in 0.5 or 1.0 formal sulfuric acid and of a platinum electrode in solutions in the same acid of cerous and ceric sulfates at various small concentrations.

The electromotive force, corrected by the usual logarithmic formula to correspond to a hydrogen gas pressure of one atmosphere and to a ratio of the cerous to ceric salt equal to unity, was found to be 1.461 volts with the 0.5 f sulfuric acid, and 1.443 volts with the 1.0 f sulfuric acid. These values were found to change only very slightly with large variations of the ratio of the concentrations of the two cerium salts, or of their total concentrations, which, however, was always kept so small as to make the ratio of cerium to hydrogen ion very small and the liquid potential of the cells insignificant.

These values cannot be exactly expressed at present on the molal hydrogen electrode standard, since the potential of hydrogen against 0.5 or 1.0 f sulfuric acid is not well known; but the value -1.44 volts is probably exact within ±0.01 volt for the reduction potential on that standard of cerous and ceric sulfates in 1.0 formal sulfuric acid in terms of the total concentrations of trivalent and quadrivalent cerium (not of their ions). It is noteworthy that this reduction potential for the ceric–cerous potential is nearly the same as the potential (-1.48 volts) derived[9] for the molal potential of Mn^{++}, $MnO_4^- + 8H^+$.

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[9] From the data of Brown and Tefft, THIS JOURNAL, **48,1128** (1926), and of Tower, *Z. physik. Chem.*, **32,568** (1900), as computed by Gerke, "International Critical Tables," 1929, Vol. VI, **p. 332.**

[CONTRIBUTION NO. 645 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

ACTIVITY COEFFICIENTS OF ELECTROLYTES. V. THE PRINCIPLE OF SPECIFIC INTERACTION IN CADMIUM AMD MAGNESIUM SULFATE AND CHLORIDE SOLVENTS

BY HAROLD B. FRIEDMAN AND VICTOR K. LA MER

RECEIVED NOVEMBER 7, 1930 PUBLISHED JANUARY 12, 1931

In two recent papers[1,2] from this Laboratory, it has been demonstrated that the principle of specific interaction, which Bronsted has shown to be valid for low valence types of solvents, can be extended to solvents containing higher valence types of strong electrolytes, provided the ratios of the ionic strengths of the two solvents of different valence types remain unaltered on varying the common solvent ion at the same equivalent concentration. Such a restriction is demanded by the Debye–Hückel theory. It is remarkable that Bronsted's principle was found to be valid in complex mixtures where the Debye–Hückel equations are incapable of accounting for the results.

In the first paper cited this aspect of the principle was tested by comparing the solubility ratios of the saturating salt thallous iodate, and also lanthanum iodate, when the anion of the solvent salt was changed from sulfate to chloride at 0.1 N concentrations. The significant ratios were usually constant to 0.2% (maximum 0.6%) in the presence of potassium or sodium as cation. In the specific case of lanthanum iodate the ratios for $(SO_4/Cl)K$ and $(SO_4/Cl)Na$ were 2.045 and 2.094, respectively, data which confirm the principle in a striking manner.

The corresponding $(SO_4/Cl)Mg$ ratio was 1.723 but since the ionic strength ratio for (SO_4/Cl) is different in the presence of magnesium as contrasted with potassium and sodium at the same equivalent concentration, the ratio in the presence of magnesium cannot be expected to equal that in the presence of potassium or sodium.

On the other hand the (SO_4/Cl) ratios for magnesium salts should be the same as for the cadmium salts, if both behave as strong electrolytes, for any given saturating salt and for two saturating salts with a common anion like thallous iodate and lanthanum iodate the (Mg/Cd) ratios should be identical for both saturating salts irrespective of the common anion of the solvent salts.

Since it is generally recognized that cadmium chloride is abnormal in its behavior as a strong electrolyte as judged by transference, conductance and osmotic measurements, a comparison of the (SO_4/Cl) solubility ratios in the presence of Mg and of cadmium is of interest since a comparison of the same ratios in the presence of potassium and sodium has demonstrated the validity of the principle involved.

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[1] La Mer and Goldman, THIS JOURNAL, **51**, **2632** (1929).

[2] La Mer and Cook, *ibid.*, 51, **2622 (1929).**

Experimental

The reader is referred to the previous publications[2] of this series for the details of the preparation of the thallous iodate and lanthanum iodate and the apparatus used in making the solubility measurements. The magnesium sulfate solutions were prepared by weighing out twice recrystallized salt dried to the anhydrous state. The magnesium and cadmium chloride solutions were prepared by diluting to 0.1 N solutions whose strength had been determined by titration for chloride content by the Mohr method.

Cadmium sulfate crystals recrystallized from J. T. Baker's c. p. salt were analyzed electrolytically and found to conform to the formula $CdSO_4 \cdot H_2O$.[3]

The experimental results are summarized in Table I. The quantities after the ± signs refer to the arithmetic mean of the deviations from the average of the individual data. The ratios computed in Table II should therefore be precise to about 1%. The so-called ideal values for the ratios are calculated from the Debye–Hückel limiting law and are submitted only

TABLE I

SUMMARY OF SOLUBILITIES OF THALLOUS IODATE AND OF LANTHANUM IODATE IN *0.1* NORMAL AQUEOUS SOLVENTS AT 25° IN MICROMOLES (10^{-6} M./L.) PER LITER

Solvent	Detns.	Soly. of $TlIO_3$ in mole/liter X 10^6	Detns.	Soly. of $La(IO_3)_3$ in mole/liter X 10^6
H_2O	*5*	*1819 ± 6*	*5*	*939.1 ± 1 2*
$MgSO_4$ *(0.05 M)*	*8*	*2625 ± 7*	*4*	*3010 ± 4*
$CdSO_4$ (*.05 M*)	*5*	*2798 ± 3*	*5*	*3205 ± 9*
$MgCl_2$ (*.05 M*)	*5*	*2755 * 9*	*6*	*1768 * 7*
$CdCl_2$ (*.05 M*)	*4*	*2708 ± 2*	*4*	*1689 * 6*

TABLE II

SOLUBILITY RATIOS AT *0.1* N CONCENTRATIONS AT 25°

Cation present	SO_4/Cl	Ideal value	Anion present	Mg/Cd	Ideal value
		$TlIO_3$ as Saturating Salt			
Mg	0.953	1.072	SO_4	0.938	1.000
Cd	1.033		Cl	1.017	
		$La(IO_3)_3$ as Saturating Salt			
Mg	1.703	*1.232*	SO_4	0.939	1.000
Cd	*1.898*		Cl	1.047	

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[3] The details of this procedure have been worked out by Mr. W. G. Parks and will be submitted shortly for publication. The method is precise to 0.01%. This work which deals with the e. m. f. of the cell $Cd(Hg)–CdSO_4(m)–PbSO_4–Pb(Hg)$ shows that cadmium sulfate is virtually completely ionized at least up to *0.01* m, since the activity coefficients of cadmium sulfate can be accurately accounted for between $m = 0.0005$ to $m = 0.01$ by the Gronwall, La Mer and Sandved [*Physik.Z.*, *29*,*358* (1928)] extension of the Debye–Hückel theory using a constant value of *3.6* Å. for the single parameter "a," and the assumption that the dielectric constant is equal to that of pure water. If cadmium sulfate is incompletely dissociated, the influence of this factor is inappreciable up to *0.01* m when electrostatic influences are properly calculated.

as a guide to the extent to which the ratio deviates from the ideal limiting value. Only those ratios having the same ideal value should be identical according to the restatement of the principle of specific interaction

The fact that $(Mg/Cd)SO_4$ ratios for thallous iodate arid lanthanum iodate are sensibly identical, *i. e.*, 0.938 and 0.939, is most gratifying. The $(SO_4/Cl)Mg$ ratios, however, are uniformly 1% lower than are the values previously reported by La Mer and Goldman.[1] Aside from possible inaccuracies in the determination of the solubilities, this is most likely to be ascribed to possible constant error in determining the chloride concentration of the solvents to be 0.1 N by the Mohr methods. Unfortunately we have not had an opportunity to repeat this phase of the work to establish the source of this 1% discrepancy Granting, however, even this limit of uncertainty, it seems very improbable that the 8 and 11% differences in the (SO_4/Cl) Mg ratio as compared to the $(SO_4/Cl)Cd$ ratio for the two saturating salts can arise from analytical error alone. We therefore conclude that the specific interaction principle does not hold when considering such an atypical electrolyte as cadmium chloride, though in view of the marked abnormality which this salt exhibits it is surprising that the principle holds as well as it does.

NEW YORK, N Y.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE HYDROLYSIS EQUILIBRIA OF TRIPHENYLCHLOROMETHANE AND TRIPHENYLBROMOMETHANE. THE FREE ENERGY OF SOME REACTIONS OF TRIPHENYLCHLOROMETHANE, TIUPHENYLBROMOMETHANE AND TRIPHENYLCARBINOL

BY J. O. HALFORD

RECEIVED NOVEMBER 10, 1930 PUBLISHED JANUARY 12, 1931

The standard free energy of a reaction is related to the equilibrium constant by the familiar equation, $AF^o = -RT \ln K$, and the two functions may be taken as alternative expressions of the tendency of the reaction to take place. However, the standard free energy is more significant, since it is related more directly to the fundamental properties of the substances involved in the reaction, and permits a wider application of the results. One advantage is that the intention to express results as free energies usually leads to experiments so carried out that the data may be applied not only to the reaction measured but to a number of related reactions as well. Certain difficulties may arise as a result, for with a given reaction the conditions most favorable to the production and measurement of equilibrium are not, in general, the best conditions for the determination of free energy relations. This is particularly true of organic equilibria, of which many are known, but few have been measured in such a way as to permit wide application of the results. Organic equilibria are usually established most readily in the liquid phase at high concentration and at elevated temperatures, while the best conditions for their interpretation in the more general form are dilute solutions in which reaction is very slow, and temperatures low enough to permit accurate regulation, sampling and analysis. The type of procedure to be employed and the method of interpretation of the results are illustrated by the work of Lewis and Burrows[1] on the free energy of urea, and that of Branch,[2] on the free energy of formic acid.

The reactions studied in this work have been selected as among the more rapidly established of the known organic equilibria, and it is suggested that for a given type reaction, experimental conditions will be determined most readily by studying first those cases which, regardless of complexity of structure of the compounds involved, will permit the simplest experimental procedure.

When a triaryl carbinol reacts with an acid, the resulting compound of the triarylmethyl with the acid radical may be a substance of the un-ionized type, such as triphenylchloromethane, or of the ionized type, such as triphenylmethyl sulfate. This has been discussed recently by Hantzsch and Buroway.[3] The type of molecule obtained depends on the nature of the acid and of the triaryl carbinol, and also upon the solvent employed. The two processes are represented by the following equations

$$R_3COH + HX = R_3CX + H_2O \qquad (1)$$

$$R_3COH + H^+ = R_3C^+ + H_2O \qquad (2)$$

The extent to which Reaction 2 takes place should be independent of the particular strong acid used, and is known to vary greatly with the triaryl radical involved. Triphenylcarbinol is converted to an ionized salt only by high concentrations of sulfuric and perchloric acids, while the methoxytriphenylcarbinols enter into this type of reaction in the presence of dilute aqueous solutions of any of the strong acids. Measurements of the basicity of the triaryl carbinols, as carried out by Lund and others,[4] are quantitative studies of this type of reaction.

Equation 1 is typical of the action of hydrochloric or hydrobromic acid on the more weakly basic carbinols, and apparently no analogous reaction with the strong oxygen acids is known. The extent to which this reaction takes place depends primarily on the stability of the compound R_3X, and although, as has been stated, a considerable amount of quantitative data is available on reactions of type 2, very little of

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[1] Lewis and Burrows, THIS JOURNAL, 34, 1515 (1912).

[2] Branch, *ibid.*, 37, 2316 (1915).

[3] Hantzsch and Buroway, Ber., 63, 1181 (1930).

[4] Lund, THIS JOURNAL, 49, 1346 (1927); Baeyer and Villiger, Ber., 35, 1189 (1902)

specific information has been obtained on the tendency toward the production of the un-ionized type of molecule. It should be interesting to study the effect of substitutions in this case, to set. if an increased tendency toward the production of the ionized salt is accompanied by a change in the tendency of the un-ionized substance to form.

The material presented in this paper includes the development of the method of measurement, its application to the equilibria in the formation and hydrolysis of triphenylchloromethane and triphenylbromomethane, and some results obtained by combining these data with other known thermal constants. The method of measurement takes into account the fact that a typically organic solvent, such as benzene, should be the best medium for the formation of the un-ionized substance, and the results will be more readily interpreted if conditions are such that the activity and free energy of the water and acid are known. With these points in mind, equilibrium was studied in a two-phase system, a benzene phase in which the triphenylcarbinol and triphenylhalogenomethane were dissolved, and an aqueous phase containing the acid.

A benzene solution containing a known concentration of the carbinol or carbinol halide was shaken in contact with an aqueous solution of the halogen acid of such a strength that at equilibrium measurable concentrations of carbinol and halide were produced. The concentration of halide was measured by titration with alkali in the presence of alcohol, and that of the carbinol was obtained by difference. In each case the aqueous layer was tested for the presence of the carbinol salt by neutralization and dilution, but no evidence of its formation was obtained.

The Hydrolysis of Triphenylchloromethane.—The results are summarized in Table I, in which the first column shows the initial concentration of triphenylcarbinol or triphenylchloromethane, and indicates the direction in which equilibrium was approached, the second the concentration, in weight per cent., of the acid in the aqueous layer, the third the concentration, in moles per 1000 g. of solvent, of triphenylchloromethane after reaction, the fourth and fifth the partial pressures of hydrogen chloride and water, taken from the "International Critical Tables,"[5] the sixth, the ratio $p(\mathrm{HCl})m(\mathrm{carbinol})/p(\mathrm{H_2O})m(\mathrm{chloride})$, and the last the time in days through which reaction was allowed to proceed. The reaction under these conditions is very slow and, since only one pair of solutions came to equilibrium, the results would be inconclusive except for the method of checking shown in the following paragraphs. The fact that equilibrium was reached only in the presence of the highest acid concentration suggests catalysis by the acid.

The equilibrium constant is taken as the mean of the two values obtained

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[5] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 301.

Table I

The Hydrolysis of Triphenylchloromethane in Benzene at 25° by Aqueous Hydrochloric Acid

Initial solution	HCl, wt., %	m $(C_6H_5)_3CCl$	p (HCl), mm. Hg	p (H_2O), mm. Hg	K	Time, days
0.193 M $(C_6H_5)_3CCl$	21.65	0.110	0.56	12.9	0.032	15
	24.20	.158	1.75	11.2	.034	5
	25.90	.176	3.5	10.0	.034	4
	26.60	.172	4.3	9.5	.0523	3
0.206 M $(C_6H_5)_3COH$	24.20	.138	1.75	11.2	.077	7
	26.60	.185	4.3	9.5	.0514	4

with 26.6% acid. The data of Table I may be summarized as follows. For the reaction

$$(C_6H_5)_3CCl \text{ (in benzene)} + H_2O(g) = (C_6H_5)_3COH \text{ (in benzene)} + HCl(g);$$

$$K_{298} = 0.0518;\ \Delta F^\circ_{298} = 1755 \text{ cal.} \quad (3)$$

Here the standard free energy refers to the gases at one atmosphere pressure and the solutes at equal concentrations or mole fractions.

The Hydrolysis of Triphenylchloromethane in the Presence of Solid Triphenylchloromethane and **Triphenylcarbinol.**—If a large excess of the solid phases is kept in contact with aqueous hydrochloric acid, the acid concentration should reach a definite equilibrium value which depends only on the temperature. In order to establish this equilibrium it is necessary to add to the system enough benzene or petroleum ether to give a non-aqueous reaction medium, and to start with a concentration of acid not far different from the equilibrium value, for relatively large quantities of the organic materials produce by reaction only small changes in the acid concentration. Apparent equilibria may be reached, due to coating of one of the solid phases, and a measurement is acceptable only when it has remained constant for several days after the addition of fresh portions of each of the solids. The hydrochloric acid solution which at 25° remains unchanged in contact with solid triphenylchloromethane and triphenylcarbinol was found to contain 24.82% of hydrogen chloride. Whence, for the reaction

$$(C_6H_5)_3CCl(s) + H_2O(g) = (C_6H_5)_3COH(s) + HCl(g);$$

$$K_{298} = 0.2195,\ \Delta F^\circ_{298} = 900 \text{ cal.} \quad (4)$$

The Solubility and Free Energy of Solution of Triphenylchloromethane, Triphenylbromomethane and Triphenylcarbinol in Benzene.—In order to show the relation between Equations **3** and 4, the free energy of solution of each of the solids must be determined. This requires measurement of the solubility and of the change of activity with concentration from the working concentration to the saturated solution. This was effected by measuring the vapor pressure lowering of benzene by the solute. The solution was introduced into a bulb to which a closed arm mercury manometer had been sealed. The apparatus was evacuated repeatedly until consistent readings were obtained with a cathetometer sensitive to 0.2 mm. Meniscus correction was minimized by taking all readings, including that with pure benzene, against the same manometer, and making frequent observations of the character of the meniscus. The temperature was constant to 0.01°. The analysis for triphenylchloromethane or triphenylbromomethane, carried out after the measurement, depended on the acid produced by hydrolysis. Triphenylcarbinol was determined as residue after evaporation of the benzene. When the residue was dissolved in acetone and the evaporation repeated, a slightly smaller figure was obtained. This was accepted as correct. The pressure readings with triphenylbromomethane were not reproducible, and the depressions were about half as large as those calculated from Raoult's law. Table XI shows the results of the measurements. The approximation to Kaoult's law was sufficiently close, in the solutions of triphenylchloromethane and triphenylcarbinol, for the present purpose, and only a few measurements were required. The first column shows the substance, the second the mole fraction of the solute, the third the vapor pressure lowering, the fourth the value calculated from Raoult's law, and the last the solubility in g. per 100 g. of benzene.

TABLE II

SOLUTIONS OF TRIPHENYLCHLOROMETHANE, TRIPHENYLBROMOMETHANE AND TRIPHENYLCARBINOL IN BENZENE; SOLUBILITY AND VAPOR PRESSURE LOWERING AT 25°

Substance	N_2	Δp (mm. Hg.)	Δp (Raoult's law)	Solubility
$(C_6H_5)_3CCl$	0.1938	20 6	19.0	85.8
$(C_6H_5)_3CCl$	.0624	6.2	5.9	
$(C_6H_5)_3CBr$	.0843			39.5
$(C_6H_5)_3COH$	.0472	5.3	4.6	16.5

Since, for the equilibria under consideration, the deviations from Raoult's law tend to cancel, the free energy of each of the substances in solution is assumed to be a simple logarithmic function of the mole fraction. For the reactions

$$(C_6H_5)_3CCl(s) = (C_6H_5)_3CCl \text{ (in benzene, } N_2 = 0.0724); \ \Delta F^\circ_{298} = -576 \text{ cal.} \quad (5)$$

$$(C_6H_5)_3COH(s) = (C_6H_5)_3COH \text{ (in benzene, } N_2 = 0.0724); \ \Delta F^\circ_{298} = 261 \text{ cal.} \quad (6)$$

By combining Equations 4, 5 and 6, a check on Equation 3 is obtained. The value of the free energy is 1737 cal. sufficiently closely to justify the interpretation of the equilibrium data. In subsequent calculations the value 1750 will be used. By combining the above equations with the appropriate free energies from Lewis and Randall,[6] the results may be expressed in the following forms

$$(C_6H_5)_3CCl(s) + H_2O(1) = (C_6H_5)_3COH(s) + H^+ + Cl^-; \ \Delta F^\circ_{298} = -5722 \text{ cal.} \quad (7)$$

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

$(C_6H_5)_3CCl$ (in benzene) $+ H_2O(l) = (C_6H_5)_3COH$ (in benzene) $+ H^+ + Cl^-$;
$AF^\circ_{298} = -4872$ cal. (8)

$(C_6H_5)_3CCl(s) + {}^1/_2O_2(g) + {}^1/_2H_2(g) = (C_6H_5)_3COH(s) + {}^1/_2Cl_2(g)$;
$\Delta F^\circ_{298} = -30{,}915$ cal. (9)

$(C_6H_5)_3CCl$ (in benzene) $+ {}^1/_2O_2(g) + {}^1/_2H_2(g) = (C_6H_5)_3COH$ (in benzene) $+ {}^1/_2 Cl_2(g)$;
$\Delta F^\circ_{298} = -30{,}065$ cal. (10)

The Hydrolysis of **Triphenylbromomethane.**—Constant boiling hydrobromic acid was found after two distillations to be sufficiently free from bromine. Preliminary measurements indicated that the optimum concentration was in the neighborhood of 41%, and this was readily obtained by diluting the constant boiling acid. Triphenylbromomethane was prepared by the action of acetyl bromide on triphenylcarbinol, and its analysis showed 99.6% purity. Benzene solutions of the carbinol and bromide containing 0.2 mole per 1000 g. of solvent were shaken with 41% hydrobromic acid. It was found necessary to exclude strong light from the reaction mixtures, because of a tendency to form triphenylmethyl peroxide and liberate bromine. This reaction will be discussed in another communication. Equilibrium was reached after fourteen days. The results are not as accurate as those with triphenylchloromethane, due mainly to the character of the available vapor pressure or activity data on strong solutions of hydrobromic acid. Starting with the triphenylbromomethane solution the equilibrium constant was 6.5×10^{-4}, and for the reverse reaction, 7.7×10^{-4}. For the reaction

$(C_6H_5)_3CBr$ (in benzene) $+ H_2O(g) = (C_6H_5)_3COH$ (in benzene) $+ HBr(g)$;
$OF,'',, = 4310$ cal. (11)

The error in the above result is probably not more than 100 calories.

The following forms of expressing the result are of interest

$(C_6H_5)_3CBr$ (in benzene) $+ H_2O(l) = (C_6H_5)_3COH$ (in benzene) $+ H^+ + Br^-$;
$\Delta F^\circ_{298} = -5690$ cal. (12)

$(C_6H_5)_3CBr$ (in benzene) $+ {}^1/_2O_2(g) + {}^1/_2H_2(g) = (C_6H_5)_3COH$ (in benzene) $+$
${}^1/_2Br_2(l)$; $\Delta F^\circ_{298} = -37{,}660$ cal. (13)

Preparation of Triphenylchloromethane from **Triphenylcarbinol.**—The standard procedure effects the conversion by the action of acetyl chloride or dry hydrogen chloride on the carbinol in ether or benzene. The data of Equation 4 and Table II suggest the following modification. The carbinol and about twice the amount of benzene required to dissolve the chloride to be formed are placed in a flask or separatory funnel and an equal volume of concd. hydrochloric acid is added. The progress of the reaction may be observed as the mixture is shaken. The excess carbinol goes into solution in a few minutes. At this point the hydrochloric acid is drawn off and replaced, the shaking is continued for a few minutes and the benzene layer is separated and dried over calcium chloride. After drying, part of the benzene is removed by distillation on the steam-bath, and crystallization obtained by the addition of petroleum ether. Triphenylchloromethane melting at 112–113° was prepared from the carbinol by this procedure in 90% yield. A similar preparation in ether solution was carried out by Baeyer and Villiger.[7]

The Reaction of Triphenylchloromethane with Hydrogen Bromide and with Bromine.—Subtracting Equation 11 from Equation **3** shows the feasibility of replacing chlorine by bromine by the action of hydrogen bromide in benzene solution

$$(C_6H_5)_3CCl\text{ (in benzene)} + HBr(g) = (C_6H_5)_3CBr\text{ (in benzene)} + HCl(g);\quad \Delta F^\circ_{298} = -2560\text{ cal.} \qquad (14)$$

This reaction will probably take place in either direction because of the ease with which a stream of gas from a generator will carry away the gas which is formed.[8]

For the reaction of triphenylchloromethane with bromine, from Equations 10 and 13

$$(C_6H_5)_3CCl\text{ (in benzene)} + {}^1/_2Br_2(l) = (C_6H_5)_3CBr\text{ (in benzene)} + {}^1/_2Cl_2(g);\quad \Delta F^\circ_{298} = 8080\text{ cal.} \qquad (15)$$

showing a strong tendency for chlorine to replace bromine in the compound.

The Reaction of Triphenylchloromethane with Bromide Ion and with Metallic Bromides.—The equations follow

$$(C_6H_5)_3CCl\text{ (in benzene)} + Br^- = (C_6H_5)_3CBr\text{ (in benzene)} + Cl^-;\quad \Delta F^\circ_{298} = 820\text{ cal.} \qquad (16)$$

$$(C_6H_5)_3CCl\text{ (in benzene)} + AgBr(s) = (C_6H_5)_3CBr\text{ (in benzene)} + AgCl(s);\quad \Delta F^\circ_{298} = 4282\text{ cal.} \qquad (17)$$

$$(C_6H_5)_3CCl\text{ (in benzene)} + HgBr(s) = (C_6H_5)_3CBr\text{ (in benzene)} + HgCl(s);\quad \Delta F^\circ_{298} = 3940\text{ cal.} \qquad (18)$$

Equation 16 states that in benzene solution in contact with an aqueous layer containing bromide and chloride ions at unit activity, equilibrium is established when the concentration of triphenylchloromethane is about three times that of triphenylbromomethane. According to Equation 17, if triphenylbromomethane in benzene is kept in contact with silver chloride, a 99.9% conversion to triphenylchloromethane should occur. This is consistent with the results of Gomberg and Cone, who found that the bromine in a number[9] of related compounds was replaced by this procedure.

The Relative Dissociation Tendency of Triphenylchloromethane and **Triphenylbromomethane.**—Equation 15 may be considered as the difference of two reactions of dissociation

$$(C_6H_5)_3CCl\text{ (in benzene)} = (C_6H_5)_3C + {}^1/_2\,Cl_2(g),\text{ and} \qquad (19)$$

$$(C_6H_5)_3CBr\text{ (in benzene)} = (C_6H_5)_3C + {}^1/_2Br_2(l) \qquad (20)$$

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[7] See Gomberg, *Ber.,* 35,2404 (1902).

[8] Straus, *Ann.,* **363,** 323 (1909).

[9] Gomberg, Ref. 7; Gomberg and Cone, THIS JOURNAL, 33,531 (1911)

.Although the individual equilibrium constants are not known, the ratio K_{19}/K_{20} is the constant of Equation 15, namely 10^{-6}, indicating that under comparable conditions in benzene the dissociation of the bromide is 10^6 times that of the chloride.

Similarly, Equation 16 may be divided into two ionic dissociations

$$(C_6H_5)_3CCl \text{ (in benzene)} = (C_6H_5)_3C^+ + Cl^-, \text{ and} \qquad (21)$$
$$(C_6H_5)_3CBr \text{ (in benzene)} = (C_6H_5)_3C^+ + Br^- \qquad (22)$$

The interpretation in this case is less definite, because the free energies of aqueous chloride and bromide ions were used in the original equation, and the result is of more interest if applied to non-aqueous solutions. Strictly, it means that a benzene solution of triphenylbromomethane in contact with aqueous bromide ion at unit activity should produce in either phase three times the concentration of triphenylmethyl ions developed by an equally strong benzene solution of triphenylchloromethane in contact with aqueous chloride ion at unit activity. Since, however, the work of transferring bromide and chloride ions from one medium to another is probably about the same, one may conclude that in benzene, and probably in other solvents as well, triphenylbromomethane has the slightly greater tendency to dissociate into ions. The conductance measurements of Walden,[10] made in liquid sulfur oxide, show a difference somewhat larger than the factor of three which may be estimated from Equation 18.

Summary

1. Data are presented on the equilibria in the hydrolysis of triphenylchloromethane and triphenylbromomethane in benzene by aqueous hydrochloric and hydrobromic acids.

2. The solubilities of triphenylchloromethane, triphenylbromomethane and triphenylcarbinol in benzene have been measured, and some data on the lowering of the vapor pressure of benzene by these substances have been obtained.

3. The results, expressed as free energies, have been combined with other free energy data to give information about the reaction of triphenylchloromethane with hydrogen bromide, bromine, silver bromide and mercurous bromide. The relative tendencies of triphenylchloromethane and triphenylbromomethane to dissociate into ions and neutral molecules have been discussed.

ANN ARBOR, MICHIGAN

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[10] Walden, Z. *physik. Chem.*, **43**, 454 (1903).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

THE CATHODE RAY TUBE IN X-RAY SPECTROSCOPY AND QUANTITATIVE ANALYSIS

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RECEIVED NOVEMBER 12, 1930 PUBLISHED JANUARY 12, 1931

The methods of x ray spectroscopy have for several years proved of value in their application to chemical analysis. The lines in an x-ray series are so few as to obviate the confusion that sometimes arises in the case of the complex arc and spark spectra. Qualitative analysis by means of x-ray spectra is simple and direct. Quantitative analysis, based on measurements of line intensity, involves a knowledge of the influence of several factors upon the intensity. It has been used with well-known success in certain special cases and is capable of general application for elements of higher atomic number than fluorine.

Hitherto two tnethods have been in vogue that involve excitation. According to the first, the sample to be analyzed is made the target in an x-ray tube, as by rubbing it onto the surface of the anode. It was in this way, for instance, that Hevesy and Coster[1] detected hafnium and the subject has been pursued still more recently.[2]

The second method may be denominated fluorescent, as it involves exciting the x-ray spectra of a sample placed outside of the x-ray tube by allowing radiation from the latter to fall upon it. Experiments with this method have been discussed by Schreiber and by Hevesy, Rohm and Foessler.[3] The latter article is noteworthy for its tables of "comparison elements" which may suitably be added to the sample as a calibrating medium for the analysis of any particular element.

It is the purpose of the present paper to describe a third method according to which the x-ray spectrum of a sample is excited directly by allowing the electrons from a cathode ray tube to impinge upon it as target. The possibility of doing this has been known and a paper has in fact been published showing that it is possible to get sufficient energy from such a tube to allow of recording photographically a spectrum line.[4] Another purpose is to present information on the use of an ionization chamber and a vacuum tube amplifier as a means of registering the spectral lines and recording their intensity. In all quantitative work hitherto which has come to our attention, the lines of the spectra have been recorded photographically and their intensities measured with a microphotometer. We have used this

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[1] Hevesy and Coster, *Nature*, 111, 79 (1923).

[2] Glocker and Schreiber. *Ann. Phys*, 85, 1089 (1928); Schreiber, *Z. Physik*, 58, 615 (1929); Eddy and Laby, *Proc. Roy. Soc.* (London), **A124**, 249 (1929); 127, 20 (1930)

[3] Hevesy, Bohm and Foessler, *Z. Physik*, **63**, *74* (1930).

[4] Eisenhut and **Kaupp,** *ibid.*, 54, 427 (1929).

method also, but our description will deal more particularly with the ionization one because of its novelty.

The intensity of a line in an x-ray spectrum is not directly a measurement of the concentration of the element emitting that line, as compared with other elements, even when corresponding lines of the same spectrum are considered. Its relative intensity varies from the following causes. **(1)** The heating of the sample during excitation may lead to a change in relative concentration due to a greater volatility of one of the constituents.

(2) The reflecting power, R, of the crystal used as a grating varies with the wave length of the individual lines as expressed by the formula for sodium chloride[6]

$$R = 6.757 \frac{1 + \cos^2 2\theta}{\sin 2\theta} \lambda^{0.25}$$

where θ is the critical angle of reflection for a line of wave length λ.

(3) The intensity, I, depends also upon the excitation voltage, V_0, of the series to which the line belongs, according to the relationship $I = \text{const.} (V - V_0)^k$, where V is the voltage applied to the impinging electrons and k is an exponent whose value is 2, at least within a certain range of the exciting voltage.[6]

(4) Absorption by whatever media lie between the source of the x-rays and the ionization chamber or photographic film.

(5) Excitation of one element by another takes place if there is present in appreciable extent a second element of neighboring atomic number, one of whose lines is of shorter wave length than the absorption band of the first element. In this case the line of the first element is intensified and that of the second element is of course weakened as a result of its absorption.

(6) In the case of fluorescent radiation, the more remote an element is in wave length from that of the exciting radiation, the weaker will be its intensity.'

(7) The relation between intensity and blackening of the film enters, if the recording of intensity be done photographically. This depends upon the extent of absorption and accordingly upon the wave length.[8]

The simplest case for analytical treatment by x-rays is that of a binary alloy whose metals are of adjacent atomic number. . Mutual excitation is absent and the other causes of variation in intensity enumerated above may be made so small under proper choice of conditions that corrections for them can safely be applied despite some uncertainty in their exact magnitude. In other cases the Hevesy method can be used by adding a

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[5] Wagner and Kulenkampff, Ann. *Physik*, 68, 369 (1922).

[6] Lorentz, Z. *Physik*, 51, 71 *(1928)*.

[7] Compton, *Phil.* Mag., 8, 961 (1929).

[8] Dorgelo, *Physik. Z.*, 26, 756 (1925); Glocker, *Z. Physik*, 43, 827 (1927).

comparison element. This involves a preliminary calibration of synthetic mixtures of the element to be analyzed.

In the case of routine analyses of similar mixtures in which the ratio of two constituents varies, the addition of a comparison element is not necessary, a simple calibration to show the relation between intensity and composition being sufficient.

In the use of the cathode ray tube or the fluorescent method, there is the advantage that the sample may simply be exposed to radiation from an exciting tube. This saves the time of introducing it to a tube and also makes it possible better to cool the sample.

Cathode Ray Tube and High Voltage Equipment

The cathode ray tube used was of the type developed by Coolidge[9] but considerably smaller than that described by him. its aluminum window of special design had a minimum thickness of 0.013 mm. and a diameter of 6 mm., and was soldered to the opening in the anode arm Due to its small diameter, a support was unnecessary. It was designed and constructed by Mr. George Hotaling of this Laboratory and we are indebted to him for supplying us with it.

It was evacuated continuously with a mercury condensation pump to assure maintenance of a satisfactory vacuum. It is hoped that eventually these tubes can be sealed off at a good vacuum during manufacture. The window was water cooled.

The tube was operated in a vertical position. with the window uppermost and the sample placed above it at an angle of 10° to the surface of the window, an angle that was found to give the maximum intensity of x-rays in a horizontal direction. The energy of the cathode rays was sufficient to heat the sample considerably. To reduce this and at the same time to prevent oxidation of the sample, a jet of hydrogen was played over it. When the sample was a metal plate, its temperature in a current of hydrogen did not rise above about 60° under bombardment at 85 kv. and 0.2 ma., the operating conditions during an analysis. When cadmium iodide, whose boiling point is 710°, was used as the sample and bombarded at 88 kv. in air without cooling, it sublimed in heavy clouds at 0.4 ma., slightly at 0.3 ma. and imperceptibly at 0.25 ma. It is readily possible, of course, to use much more rigid cooling wherever desired, such as cooling water or ice or liquid air placed upon the sample.

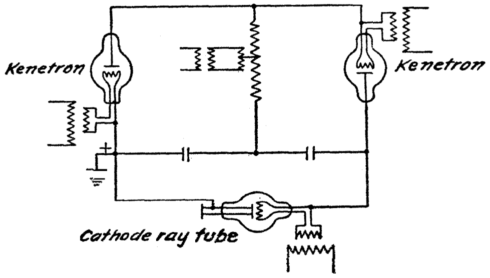

Fig. 1.—Diagram of high voltage set.

The tube was operated by a high voltage d. c. outfit to avoid heating of the window under a. c. operation by electrons of too low velocity to contribute to excitation of x-ray spectra. The circuit used is shown diagrammatically in Fig. 1: 60-cycle regulated a. c. at 110 v. was supplied from a control transformer. A 1:1 transformer, whose secondary was insulated for 100 kv., supplied an x-ray high voltage transformer, with middle points of windings connected, resting on porcelain insulators 40 cm. high. The output from

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[9] Coolidge. J. Franklin *Inst.,* 202, 693 (1926).

this was shared between two kenetrons supplying a bank of fourteen condensers, each of 2.5 mf. capacity and capable of standing about 7000 v.[10] The voltage delivered to the cathode ray tube is double that coming from the x-ray transformer as the current is alternately rectified by each kenetron and delivered to one-half of the bank of condensers. The function of the latter is to deliver a current of nearly uniform voltage—the capacity of each half being such that it may deliver energy to the tube without appreciable voltage drop during the half cycle when the rectified current is being delivered to the other half of the condensers.

The filament of the kenetron on the grounded side was lighted by a transformer of low voltage insulation; the filaments of the other and of the cathode ray tube were necessarily operated by transformers whose secondaries were insulated 100 kv. above ground.

To assure uniformity of voltage distribution along the condensers, the terminals of each were connected to a resistance of 23 megohms. This was constructed in the following manner. A long glass tube 2 cm in diameter was filled with a solution of 1 part of grain alcohol to 2.5 parts of xylol, and wire terminals sealed into it every 12 cm. were connected to the condenser terminals. The high voltage set was calibrated with 6.25-cm. brass spheres.[11]

Experiments with Ionization Chamber.—The spectrometer was made of brass in the laboratory machine shop. Reflection was from the 100 plane of a sodium chloride crystal which could be rotated by an arm about the center of a circular table, 12.5 cm. in diameter, graduated in degrees. Another arm extended 20 cm. beyond the table and carried a box containing the ionization chamber and the amplifying units. A vernier attachment allowed the crystal to be set at four minute intervals. The crystal was chosen from several specimens of halite, after many had been rejected because of surface irregularities which were either manifest to the eye or else sufficient to give distorted intensity curves.

A slit, kept at a width of 11 mm., was placed at the opening of the ionization chamber, at a distance of 12 cm. from the center of rotation. The collimating slits, whose opening was varied from 0.3 to 0.9 mm., were placed 4 and 12 cm. from the axis of the spectrometer. The front slit was 3.5 cm. from the axis of the cathode ray tube.

The brass ionization chamber was made of two concentric cylinders of 1-mm. material, 20 cm. long. The inner one served as one electrode and had a section of a cylinder soldered to the bottom. All connections to it were insulated with hard rubber. The other electrode was a 3-mm. rod with amber insulation, directly connected to the control grid. Aluminum foil, 0.015-mm. thick, was cemented across the opening.

The chamber was filled with methyl bromide. In the absence of leaks, its performance was consistent for weeks at a time. The chamber was large enough to allow of complete absorption of radiation on the long wave length side of the bromine absorption edge.

The amplifying system is shown diagrammatically in Fig. 2. The basis of it is the new four-element vacuum tube, FP-54, characterized by a very high input resistance. The operation[12] of it and of the amplifying system is based upon the facts that x-rays entering the ionization chamber produce an ionization current proportional to their in-

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[10] A brief outline of this system is given in Glocker, "Materialprüfung mit Röntgenstrahlen," p. 28, 1927, and a discussion of the condenser requirements can be found in Hull, Gen. *Elec. Review,* 19, 173 (1916).

[11] Peek, "Dielectric Phenomena in High Voltage Engineering," 1915, p. 89.

[12] Metcalf and Thompson, *Phys. Rev.,* 36, 1489 (1930); Nottingham, J. Franklin *Inst.,* 209, 287 (1930), gives a helpful discussion of similar amplifying systems, although based on three-element tubes.

tensity and that this ionization current determines the potential of the control grid of the tube. This grid potential affects the plate current and the variations in it are read on a sensitive galvanometer, with the normal initial plate current balanced out by means of an adjustable voltage. Since the characteristic curve of the tube may be considered straight within the range used, the galvanometer deflection may be taken directly as a measure of the relative intensities of the x-rays entering the chamber.

Considerable difficulty was experienced in obtaining a suitable grid resistance. Mixtures of xylol and alcohol, copper oxide fused into glass and India ink lines on paper were found to be unsatisfactory. When they were made large enough to give the required sensitivity, they polarized readily. A pencil line on hard rubber was fairly satisfactory, giving galvanometer deflections which were reasonably steady. The best resistance, however, and the one which we used in the tests described here, was one made by Dr. Lewi Tonks of this Laboratory and which he kindly loaned to us. It was made by the distillation of tungsten from a wire upon a glass fiber in an evacuated tube.

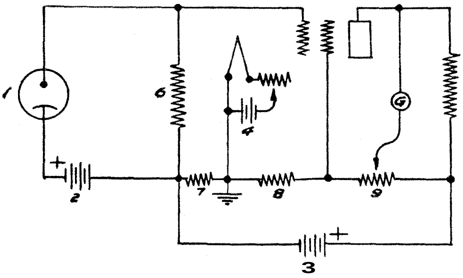

Fig. 2.—Diagram of amplifying set.

1, Ionization chamber; 2, 180-v. B battery units; 3, 12-v. storage battery; 4, 6-v. storage battery; 5, 50,000-ohm. resistance; 6, $3(10)^{10}$-ohm. grid resistance; 7–9, 500-ohm. resistances.

The sensitivity of the set may be calculated from a knowledge of the galvanometer sensitivity $S = 5.5(10)^{-10}$ amp., the mutual conductance of the tube $G_m = 21$ μa./V, the grid resistance $R = 3\ (10)^{10}$ ohms, the grid voltage V_g, the grid current I_G, and the plate current I_p.

$$G_m = I_p/V_g = S/V_g$$

Since $V_G = I_G R$, $I_G = S/G_m R = 8.7\ (10)^{-16}$ amp. This expression for the sensitivity gives the smallest measurable grid current.

As the high voltage outfit was not enclosed, adequate screening was our greatest difficulty. As the first step, to make the connection from chamber to grid as short, and at the same time as well insulated, as possible, all of the amplifying set, including the vacuum tube and resistances Nos. 5–9, was mounted with the chamber on the movable spectrometer arm in a completely enclosed wooden box lined with tin foil and covered with 2-mm. aluminum sheet and with the side toward the crystal faced with lead 3 mm. thick. The box contained calcium chloride as drying agent. The entire spectrometer was enclosed in a galvanized iron box, open at the top. The upper part of the cathode ray tube, including the window and sample, was enclosed in a lead box open at the bottom and with a small opening opposite the sample.

The flexible connection from the amplifying set to the batteries and galvanometer was enclosed in the metal casing of BX cable. The batteries, insulated on pieces of bakelite, were also enclosed with galvanized iron, and the galvanometer with a tin box. All of the metal protective enclosures were grounded and all connections soldered. Steady conditions in the amplifying system were obtained by allowing it to run for half an hour.

An approximate estimate of the sensitivity of the spectrometer was obtained from an experiment with a copper target. With the tube operating at 85 kv. and 0.2 ma., and with 0.4 mm. slits, the peak of the Kα doublet gave a net deflection of 90 cm. with an accuracy of 0.5 cm. on a scale 2.6 m. distant, corresponding to an ionization current of $3\ (10)^{-13}$ amp.

Measurements were based on the first order of the K radiation, using the intensity coming from the unresolved Kα doublet. The slit in front of the ionization chamber was kept at an opening of 11 mm., to have assurance that all of the reflected energy would enter the chamber. Actually the chamber could be turned through an angle of 2° for a particular setting of the crystal before a decrease in intensity was noticed. In practice the angle of the chamber was kept at twice the angle of the crystal, being reset for every 30' change in the latter. The curves for intensity against crystal angle were plotted on coordinate paper and the area of the doublet, lying above the continuous radiation, was measured by counting squares, as this method gave greater accuracy than a planimeter.

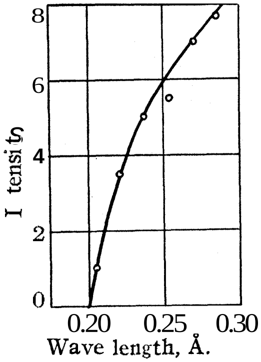

Fig. 3.—Continuous radiation curve for tungsten at 74.7 kv.

The loss in velocity of the electrons in passing through the aluminum window was determined by measuring the continuous radiation of tungsten on the short wave length side. The curve expressing the results is given in Fig. 3. The abscissas are plotted not as angular setting of the crystal, but rather as wave length, in terms of $\lambda = 5.628 \sin \Theta$. Zero radiation occurs sharply at 0.200 Å., from which the exciting voltage can be calculated as $V_0 = 12.34/\lambda = 61.7$ kv. As the window produces some straggling, this represents the optimum velocity. The potential applied to the tube was 74.7 kv. Terrill's[13] formula for the loss in velocity in aluminum foil is $v^2 - V^2 = 1.1(10)^{12}x$. If this is applied to our case, for a thickness x of 0.0013 cm. and a primary velocity v of 74.7 kv., the final velocity V should be 64.5 kv. For a final velocity of 61.7 kv., that obtained by us, the thickness should be 0.0016 cm. The latter value probably expresses better our effective loss in velocity, as the thickness of gas contributes to it and also irregularities on the surface of the window, which was made purposely non-uniform.

It seemed important to determine how the intensity of the Kα doublet varies with the voltage, not only to show the changes in the energy available for analytical purposes, but also to get a closer value for the correction factor determining the relation between line intensity, **I**, and the difference between the applied voltage, V, and the exciting voltage, V_0. This relation was expressed by Webster and Clark[14] for the K series of rhodium as $I = \text{const.} (V - V_0)^{3/2}$. Kettmann[15] and Stumpen[16] found that near the exciting voltage the exponent was 2 for the K series of chromium, copper,

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[13] Terrill, Phys. *Rev.*, 22, 101 (1923).

[14] Webster and Clark, *ibid.*, 9, 571 (1917).

[15] Kettmann, *Z. Physik*, 18, 359 (1923).

[16] Stumpen, *ibid.*, 36, 1 (1926).

molybdenum and silver, but decreased for higher voltages. Lorentz[6] studied carefully the K series of aluminum and found that the exponent was 2 up to double the exciting voltage, decreasing thereafter up to about nine-fold the exciting voltage; from that point on the intensity itself decreased.

We have made intensity measurements at 0.2 ma. on molybdenum up to four-fold the exciting voltage and on iron up to eleven-fold. In both cases the exponent remained 2 throughout the range, and there was no evidence of reaching an optimum value. The data are given in Table I. In calculating the exponent it was of course necessary to use values of the voltage which are characteristic of the optimum electron velocity at the target. This was done by means of the Terrill equation, using x = 0.0016, and is expressed in the table as "electron velocity, *V*."

The results are shown in the curves of Fig. 4. To show the extent to which they justify an exponent of 2, the intensity is plotted in Fig. 5 on log paper against $V - V_0$, using values for V_0 of 19.9 for molybdenum and 7.1

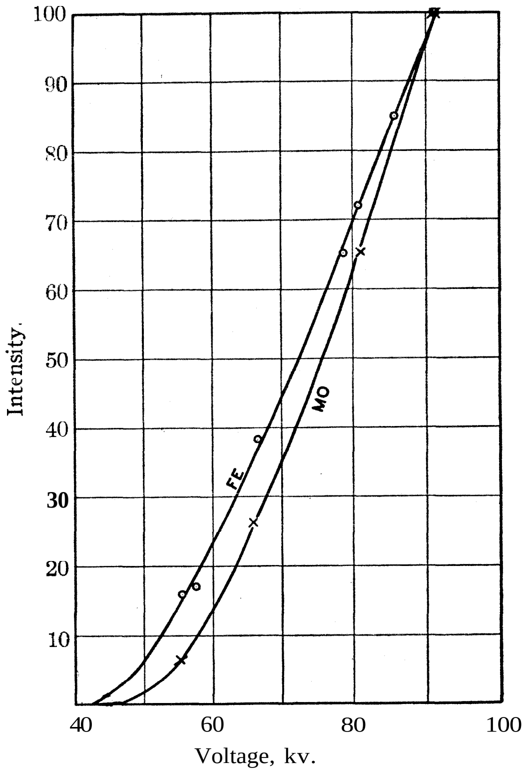

Fig. 4.—Variation of intensity with voltage for Kα doublet of iron and molybdenum.

TABLE I

EFFECT OF VOLTAGE UPON INTENSITY OF Kα DOUBLET

Applied voltage. Kv.	Electron velocity, V	Intensity *Kα* Doublet	
		Mo	Fe
90.8	80.4	100.0	100.0
85.7	74.6	..	85.0
80.8	69.0	65.4	71.9
78.7	66.6	..	65.0
66.6	51.7	..	38.0
65.8	50.8	26.4	..
57.5	39.3	..	17.0
55.2	35.9	6.4	15.8

for iron. The exponent is calculated from the slope of the curves to be **2.03** for molybdenum and 1.97 for iron, with no evidence of decreasing to lower values.

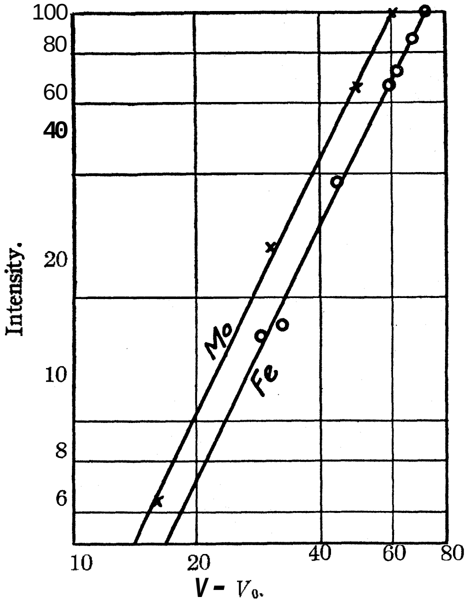

Fig. 5.—Variation of intensity of Ka doublet with $V - V_0$.

This distinction from the results of others whose experiments were with x-ray tubes may be due to the presence of a certain range of velocity in the beam coming from the cathode ray tube. At a low voltage it would accordingly excite a smaller intensity of radiation than would the electrons of uniform velocity in an x-ray tube. As the voltage increases, the difference would lessen.

The variation in intensity with current is shown in Fig. 6 for the case of the $K\alpha$ peak of molybdenum.

In the analytical work the cathode ray tube was operated at 85 kv. and 0.2 ma. The measurements were checked by repeating a run, either in whole or in part. About one hour was required for such an examination of a binary alloy. In some of the cases a further check was made by repeating the run on a different day, generally on a fresh surface of the sample. This is denoted in the tables by a separate entry.

In all cases the alloys had a polished surface and for the most part were in flat pieces which had been rolled down from stock. The composition was determined by chemical analysis which was kindly carried out for us by Dr. Dorothy H. Brophy of this Laboratory.

No high degree of accuracy

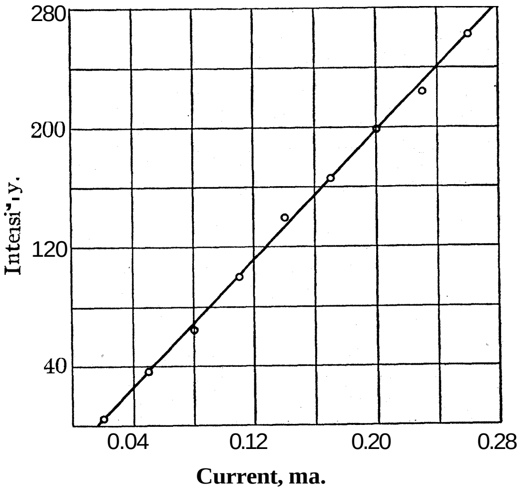

Fig. 6.—Variation of intensity with current for peak of $K\alpha$ doublet of molybdenum.

is claitned for the results found, for the aim was rather to explore the possibilities before spending too much effort in refining features of the apparatus. One of its weak features was the crystal. As already mentioned, several were discarded during preliminary work. The final one used in these experiments was not above reproach. Indeed in going over the curves after the work had been completed, it was noticed that in some of them there was still present a slight distortion at the base of the Kα doublet and that the results from these showed rather poor agreement under repetition. By chance, however, the setting of the crystal had been slightly altered at one time and the results obtained thereafter appeared more reasonable and are the ones reported below.

TABLE II

RELATION BETWEEN COMPOSITION AND INTENSITY OF Kα RADIATION FOR ALLOYS OF ADJACENT ATOMIC NUMBER; SLITS SET AT 0.30 MM.

Alloy	Composition, atomic, % Cu	Intensity, % Cu
Copper–zinc	64 5	64 6
Copper–zinc	ti4 5	84.4
Copper–nickel	4 8	6.1
Copper–nickel	39.1	33.1
Copper–nickel	64.7	65.6
Copper–nickel	94 1	93 7

The results on two binary alloys whose constituents are adjacent in atomic number are given in Table II. These represent the simplest cases, as mutual excitation is absent.

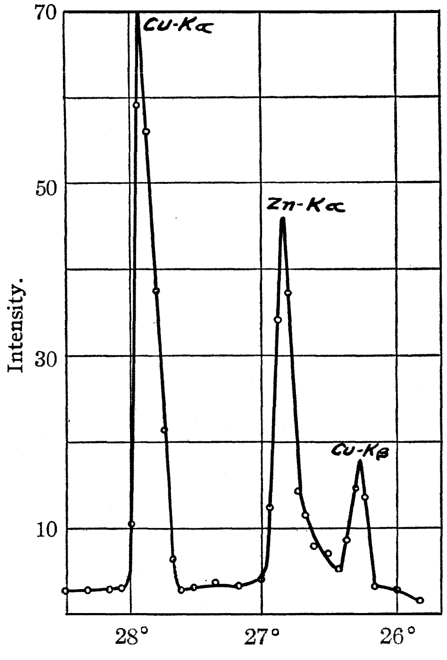

Fig. 7.—Intensity curves for copper–zinc alloy containing 64.5 atomic per cent. of copper; slits, 0.30 mm.

A typical curve from which the areas denoting intensity were measured is shown in Fig. 7. In all of them equally smooth curves could be drawn through the points denoting the observations. The angular settings noted are purely relative. Actually in all cases the angles corresponding to the peaks of the curves were found to give with reasonable accuracy the values of λ for the Kα_1 arid Kβ_1 lines. In Fig. 8 is given a curve showing for the copper–nickel alloys the relation between composition and relative intensity. Theoretically, the latter should be proportional to the atomic per cent. Actually, the effects of crystal reflectivity and of absorption by air and chamber window act to increase slightly the relative intensity of the radiation from the elements of higher atomic number. It is for this reason that in the copper–nickel alloys the relative intensity of the copper radiation runs somewhat high. The curve of Fig. 8, however, is typical of a calibration curve which could be used in analyzing an unknown. For the same reason, the relative intensity of the copper radiation from the copper–zinc alloy should be lower—the values obtained in our analysis are therefore somewhat too high.

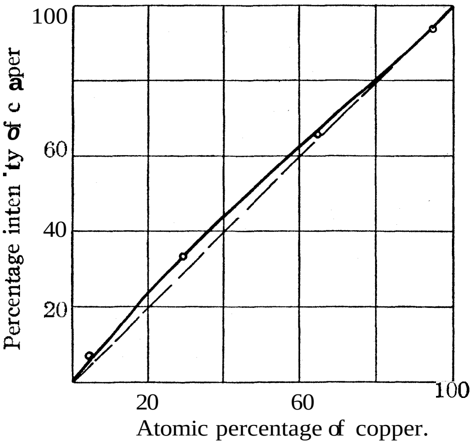

Fig. 8.—Relation between intensity of Kα doublet and composition for copper–nickel alloys.

The other case for which mutual excitation should be absent occurs for two elements whose atomic numbers are remote. Molybdenum and iron were selected and three different compositions were examined. Unfortunately, they had been made up in small samples and bad segregation had evidently occurred. Simply a resetting of the sample led to a different relationship of intensities, although for any one setting good agreement was found on repetition. The results are, therefore, of no value analytically, but they are given in Fig. 9 for an alloy to which 9.3 atomic per cent. of molybdenum had been introduced, to show the differences for the two Kα doublets. That of iron is of such long wave length, 1.932 Å., that the continuous radiation in its neighborhood is very low, whereas that of molybdenum at 0.708 Å. is near the peak in the continuous radiation curve. The intensity of the molybdenum radiation is essentially very much greater than that of iron for equal amounts of each because of its higher reflection from the crystal and greater transmission of the air and chamber window.

As illustrative of the case in which strong mutual excitation is present, the iron–nickel alloys were chosen. The Kα_1 line of nickel is at 1.654 Å.,

TABLE III

RELATION BETWEEN COMPOSITION AND INTENSITY OF Kα RADIATION FOR IRON–NICKEL ALLOYS; SLITS SET AT 0.90 MM.

Composition atomic, % Fe....	91.7	91.7	64.8	64.8	55.5	22.8	5.9
Intensity, % Fe..............	87.8	87.7	67.8	68.4	60.8	26.6	6.9

just within the absorption edge of iron, 1.738 Å., at which its K radiation is excited. The results are given in Table III.

A typical set of curves is shown in Fig. 10 and the relation between all of the alloys is given in Fig. 11. The situation is rather complicated The effect of crystal reflectivity and of absorption is to decrease the intensity of the iron, but for all alloys containing less than 80 atomic per cent. iron, the predominating effect on the intensity is the excitation produced by the nickel, accompanied, of course, by a partial absorption of the nickel radiation by the iron. In general, one would not expect this effect to be appreciable for small amounts of nickel. On applying the corrections for the first two effects and for that of voltage to the alloy containing 91.7 atomic per cent. iron, a value of 91.9% was obtained from the relative intensities.

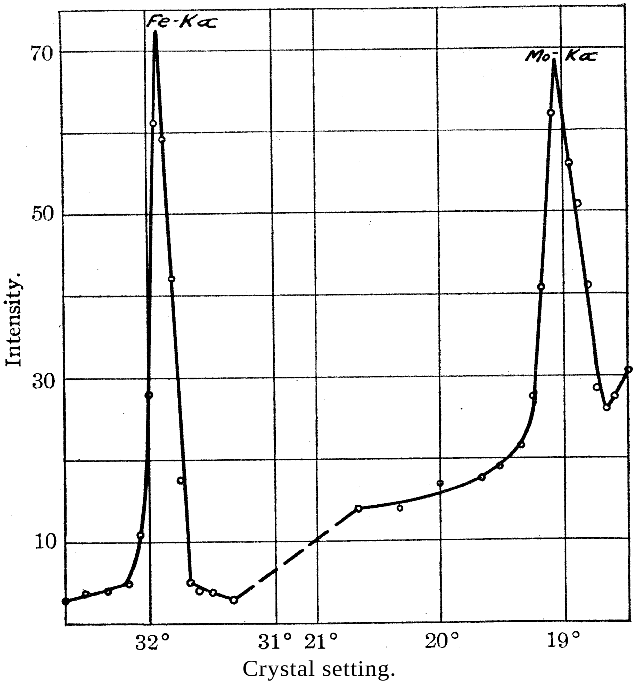

Fig. 9.—Intensity curves for molybdenum–iron alloy; slits, 0.40 mm.

Experiments with Photographic Recording.—Some experiments were also carried out on binary alloys with a Seemann spectrometer, using a crystal of sodium chloride and a wedge placed above it to form the slit. The opening of the spectrometer was placed 2–3 cm. from the window of the cathode ray tube, and the sample as before was right above the window, making a 10° angle with it.

The density of the lines on the film was measured for us by Mr. F. Ben-ford of this Laboratory by means of a mercury lamp with a Fabry and Buisson microphotometer.

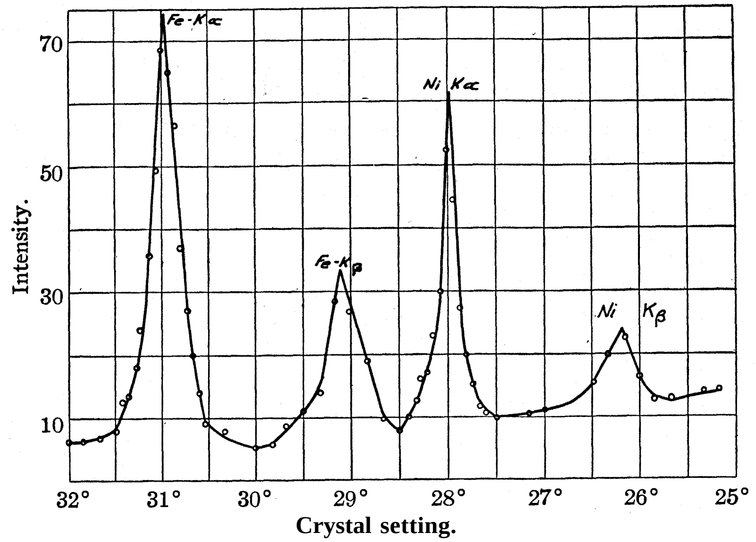

Fig. 10.—Intensity curves for iron–nickel alloy containing 64.8 atomic per cent. of iron; slits, 0.90 mm.

With the cathode ray tube at 88 kv., experiments were made with various polished binary alloys. For those containing about equal parts of metals of adjacent atomic number, silver and cadmium and tin and antimony, the spectrometer was oscillated over a 3° angle. At a slit width of 0.05 mm., sufficient to resolve the Kα doublet, the time of exposure to attain a line density in Briggs logarithms of 0.4 was eighty minutes at 0.3 ma. and 110 minutes at 0.2 ma.; with a slit of 0.50 mm., the time was reduced to forty and sixty minutes, respectively. For a single element the time required to attain the same density was sixteen minutes, using a 1° oscillation, a slit width of 0.05 mμ and a current of 0.2 ma.

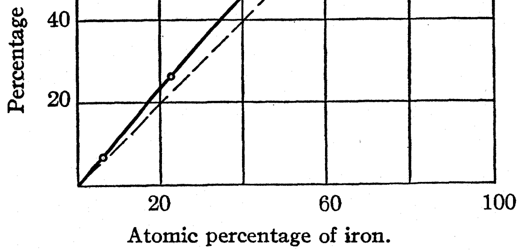

Fig. 11.—Relation between intensity of Kα doublet and composition for iron–nickel alloys.

Tests were made with the pure metals for various times to get the relation between photographic density and intensity of x-radiation, and also the relative photographic activity of the different metals. Applying this correction and the small ones for the reflecting power of the crystal and the voltage effect, a value of 59.6 atomic per cent. silver was found for a silver--cadmium alloy containing 60.2 atomic per cent., and 49.2 atomic per cent. of tin for a tin--antimony alloy containing 49.4 atomic per cent.

Conclusion

The ionization method as applied to our present apparatus was capable of detecting qualitatively about 0.5% of an element, and quantitatively 3% or more. The apparatus as described is of a preliminary nature, but it serves to show the possible scope. Even with the present cathode ray tube, some simple and obvious changes would add greatly to the effective radiation. One is operation of the tube in a horizontal position so that the excited portion of the sample would have the shape of a vertical slit, thus introducing about three-fold more energy to the chamber. Another is operation at higher voltage.

The limit of sensitivity for the amplifying set likewise is many-fold greater than for that employed by us. Even the present one would be applicable for use with the x-ray tubes described by others for quantitative work, where the energy available is so great that very much smaller percentages could be detected.

It is a pleasure for us to acknowledge the cooperation of many in the laboratory staff. We are particularly grateful to Dr. W. P. Jesse and Dr. C. W. Hewlett for the help coming from their experience with the technique of x-ray spectroscopy, to Mr. B. J. Thompson for suggestions in adjusting the amplifying set, and to Dr. A. L. Marshall in regard to the high voltage outfit.

Summary

1. The use of a cathode ray tube is described for exciting x-radiation of samples placed before its window, and also the use of an ionization chamber and an amplifying system for recording the intensity.

2. The variation in the intensity of the Kα doublet for Mo and Fe is shown to follow the relation $\mathbf{I} = c(V - V_0)^2$, up to a voltage four-fold that of V_0, the exciting voltage for Mo, and eleven-fold for Fe. The exponent accordingly remains constant over a greater voltage range than has been observed in x-ray tubes.

3. The application of the cathode ray tube to the quantitative analysis of alloys is shown by both the ionization and the photographic methods.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

PERMANGANATE DECOMPOSITION IN ALKALINE MEDIA[1]

BY R. H. FERGUSON, WM. LERCH AND J. E. DAY

RECEIVED NOVEMBER 18, 1930 PUBLISHED JANUARY 12, 1931

The purpose of this investigation was *(a)* to measure the effect of hydroxyl-ion concentration and of temperature on the rate of the reaction

$$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{=} + 2H_2O + O_2 \qquad (1)$$

and (b) to study the possible reversibility of this reaction in the absence of extraneous materials other than the reaction medium (water).

One of the authors,[2] when oxidizing ethyl alcohol by potassium permanganate solutions containing potassium hydroxide, observed that the available oxygen values of the strongly alkaline permanganate solutions were measurably lessened if not used promptly. In 1917 Day prepared a solution containing 340.8 g. of stick caustic potash (purified over alcohol), 30.404 g. of potassium permanganate and one liter of water, and kept the mixture at room temperature. By the end of one year the available oxygen had dropped 25%; in four years, 50%; and in ten years, 53%. A portion of this final dark green solution was held at 95°, manganese dioxide appearing and the supernatant liquid becoming colorless in about six days. The potassium permanganate (available oxygen = 98.67% of the theoretical) had not been aged and freed of any probable dioxide.

Preparation of Materials

Unless otherwise stated all filtrations were made through asbestos fiber supported in a Biichner funnel. The fiber was purified by digestion with sodium hydroxide, then with hydrochloric acid, and the product well washed, suspended in dilute sulfuric acid, treated with potassium permanganate solution and finally washed until free from chloride and sulfate ion.

Potassium hydroxide, when prepared by Ruby's[3] method, reduced a permanganate solution, hence the solutions of the two alkalies (potassium and sodium) used in this investigation were obtained by metathesis from purified non-reducing saturated solutions of barium hydroxide and 2 *N* solutions of the corresponding alkali metal sulfate. After reaction the decanted solutions were freed of the last traces of barium sulfate by

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[1] The results of the preliminary work leading up to this more complete investigation were presented by William Lerch to the Graduate School of the University of Wisconsin, June, 1922, in candidacy for the degree of Master of Science; and in abbreviated form at the Pittsburgh Meeting of the American Chemical Society, September, 1922. The present paper is from the dissertation presented by R. H. Ferguson to the Graduate School of The Ohio State University, June, 1927, in candidacy for the degree of Doctor of Philosophy, a digest being given at the St. Louis Meeting of the American Chemical Society, April 18, 1928.

[2] See Evans and Day, THIS JOURNAL, 38,375 (1916); *ibid.*, 41, 1267 (1919).

[3] Ruby. *ibid.*, 43, 294 (1921).

filtration in a carbon dioxide-free atmosphere. These solutions were concentrated to approximately 13 N in large loosely covered glass pyrex beakers. The final product was further appropriately treated until it gave negative tests[4] for carbonate, chloride, barium and sulfate ions. Ten-cc. samples acidulated with sulfuric acid did not reduce one drop of 0.1 *N* potassium permanganate.

A slightly less than saturated solution of potassium permanganate was placed in a clear glass-stoppered bottle and aged in ordinary light for five months, then filtered six times, at two-day intervals, through specially prepared[6] asbestos wool. An ultramicroscopic examination of the final solution showed no evidence of colloidal manganese dioxide. The last filter was tested for the presence of manganese dioxide with negative results. The dioxide test was made by first carefully washing the undisturbed filter free from potassium permanganate and then determining the oxidation titer of the filter by the oxalic acid–permanganate method.

A sodium permanganate solution was prepared from Kahlbaum's best product in the same manner as was the potassium salt except that because of the relatively greater impureness of the sodium compound, it was allowed to age for a year with six periodic filtrations through asbestos. The sixth filter gave a negative test for manganese dioxide.

These two permanganate solutions were then standardized against sodium oxalate (Bureau of Standards) and kept in stoppered black-coated bottles. The molar concentration of the potassium permanganate solution was 0.1248, this value being an approximate mean of the concentration used in an acid medium in quantitative analysis and that in an alkaline medium in organic oxidation. Because of the reputedly poor keeping quality of sodium permanganate, its concentration was brought down to 0.0680 M.

Experimental

All reactions were carried out in flasks (Fig. 1) kept in a constant temperature bath. A is a pyrex Kjeldahl flask constricted at the top. The pyrex cup E is sealed into the rubber stopper B by means of plaster of Paris, C. The collection, in the cup, of condensed steam from the reaction mixture was practically avoided by keeping the cup nearly filled with mercury, D, when the inverted 30-cm. glass condenser was in position. Care was always exercised in preventing the mercury from getting into the flask contents. The condenser was equipped with a guard tube filled with soda lime and cotton. A strip of blotting paper fastened around the condenser just above the cup E prevented condensed water vapor from the thermostat from getting into the reaction mixture by the route of the mercury seal when samples were withdrawn. The water-bath thermostats was electrically heated and was controlled to within 0.1°.

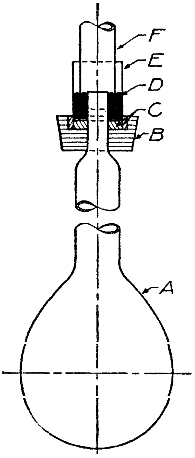

Fig. 1.

In each reaction mixture the initial strength of the potassium permanganate was 0.156 mole and that of the sodium permanganate was 0.085 mole of available oxygen per liter. Two hundred cc. of the permanganate solution of the necessary concentration was placed in the reaction flask and a like volume of the alkali solution of the desired concentration in another flask. The two solutions were then brought to the desired

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[4] Commonly accepted wet methods.

[5] Cheishvili, J. Russ. *Phys.-Chem. Soc.*, 42, 856 (1911).

[6] Day and Ferguson, "A Constant Temperature Bath," This Laboratory, 1927, unpublished.

temperature and the alkali solution added to the permanganate solution at a sufficiently slow rate to avoid entirely the precipitation[7] of any of the permanganate. After vigorous shaking for several minutes the reaction mixture was placed in the thermostat and the flask-condenser connection made as in Fig. 1. The progress of each reaction was determined by periodically measuring the amount of available oxygen in a 10-cc. portion of the reaction mixture. The reaction in the sample was stopped by the addition to the sample of a measured quantity (65 cc. for the potassium and 35 cc. for the sodium series) of a sulfuric acid solution of standard oxalic acid and this then back-titrated for the oxygen titer with standard potassium permanganate. For the 75 and 95° series the sampling pipet was brought to about the temperature of the reaction mixture to avoid volume errors.

The identity of oxygen as an evolved product from the reaction mixtures was established by the glowing splint test and also by absorption in a hydrochloric acid solution of cuprous chloride.[8] Samples of the reaction mixture after the available oxygen titer became constant were examined under the ultramicroscope for colloidal manganese dioxide.

Results and Discussion

The use of a mechanical stirrer in the reaction apparatus, described above and partially shown in Fig. 1, added greatly to the tediousness of sample withdrawal. A modified form of this apparatus, consisting of an 18-cm. glass condenser sealed to a short-necked pyrex flask, was equipped with a mechanical stirrer. In Table I is shown the relative effect of slow (60 r. p. m.) stirring (Col. 1) and no stirring (Col. 2) upon the water medium reaction between 12.4 N potassium hydroxide and 0.634 N potassium permanganate at 50°. The velocity of the reaction was increased slightly but the extent was practically the same. Because of the difficulty in effecting condensation of the water with the 18-cm. condenser as well as the added manipulation in the removal of samples for analysis, the use of this apparatus was discontinued.

TABLE I

COMPARATIVE DATA

Time, hours	Available oxygen, mole per liter Col. 1	Col. 2
0	0.156	0.156
12	.151	.152
48	.149	.149
96	.143	.145
144	.142	.143
192	.139	.142

The effect of four concentrations of potassium hydroxide and of three temperatures on the conversion of potassium permanganate into a manganese compound, or compounds, of lower manganese valence is shown in Figs. 2, 3 and 4. The molar ratios (before mixing) of permanganate to alkali are approximately 1:45, 57, 76 and 99. The behavior of sodium

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[7] Sackur and Taegener, *Z. Elektrochem.*, 18, 718 (1912).

[8] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, 1922, p. 380.

permanganate in the presence of sodium hydroxide under conditions similar to those for the two potassium compounds is presented in Figs. 5,

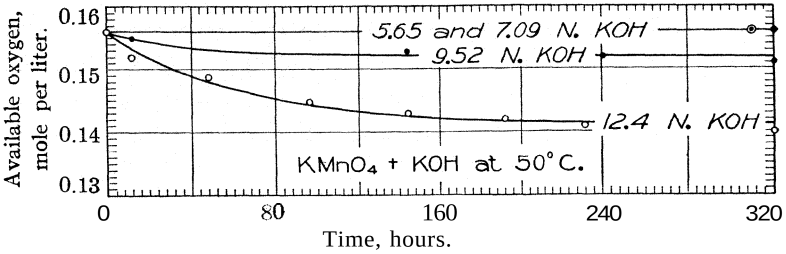

Fig. 2.

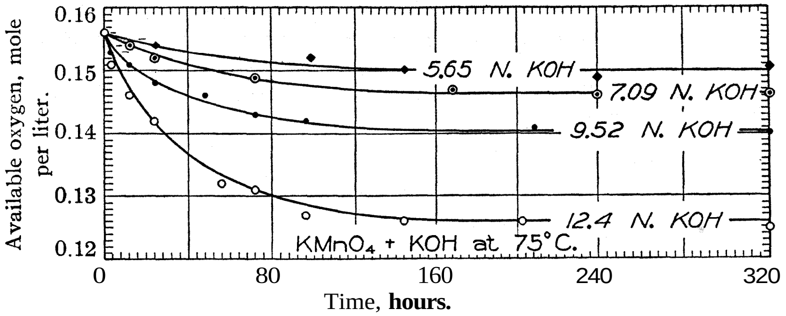

Fig. 3.

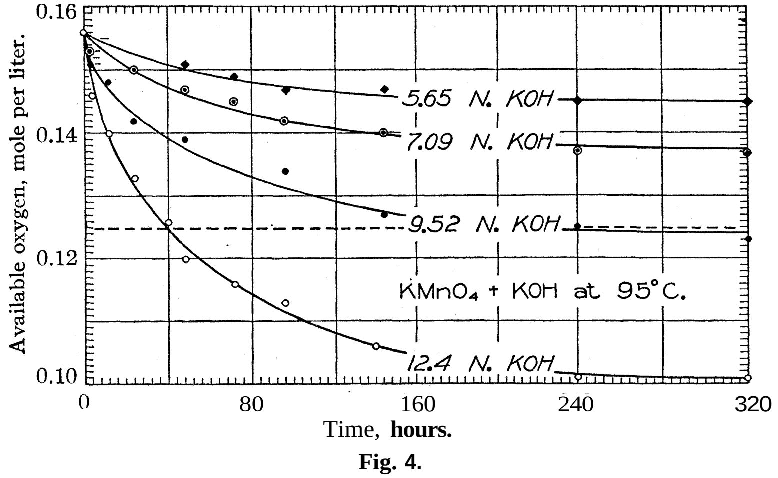

Fig. 4.

6 and 7. In the case of this permanganate, and the corresponding hydroxide, the integral molar ratios are 1:46, 60, 97 and 169. The available oxygen value is that calculated on the basis of normal solutions for oxidation–reduction in acid media.

Whether or not the dissolved glass from the extensive action of the strong alkali upon the reaction flasks at 95° may have influenced these reactions catalytically or otherwise was not studied.

Figures 2–7, inclusive, show that the extent of the loss of available oxygen is a function both of the concentration of the hydroxide and also of the temperature. There is, for each temperature, a minimum concentration of alkali necessary for a depreciation of the available oxygen in the reaction mixture. This alkali value may be roughly estimated from Figs. 2, 5 and 6. For certain alkalinities, there was either no reaction or else it was not measurable by the method used. An experiment with potassium permanganate and 12.4 N potassium hydroxide at room temperature (about 30°) for 240 hours gave no measurable loss of available oxygen.

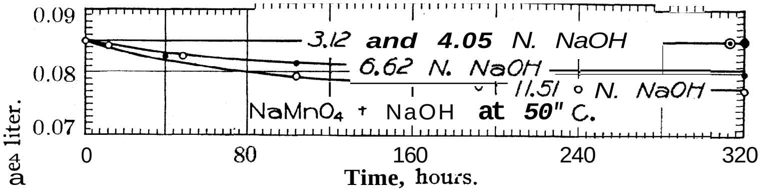

Fig. 5.

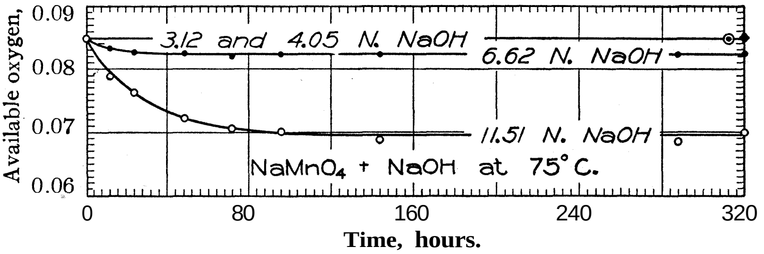

Fig. 6.

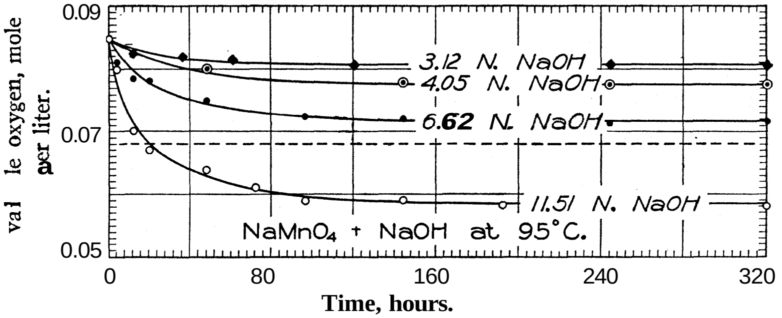

Fig. 7.

The color changes as identified by the naked eye in ordinary daylight through a north window for the potassium permanganate–potassium hydroxide reactions are given in Table II. Aliquot portions of the final and also of several of the intermediate reaction mixtures of the 9.52 and 12.4 N potassium hydroxide series at 95° were filtered through asbestos and the filters examined for any precipitate with negative results. Under the ultramicroscope samples of the intermediates showed no suspension; samples of the finals, when cooled and exposed to the air, seemingly underwent some decomposition with the formation of a suspension, hence a positive decision was impossible. A second aliquot of each of these two final solutions when diluted (1–5) with water changed in color to a pink accompanied by residue formation presumably in accordance with

TABLE II

COLOR CHANGES

Temp., °C.	Alkalinity			
	5.65 &*	7.09 *N*	9.52 *N*	12.4 *N*
50	Purple	Purple	Almost black	Black
75	Purple	Darker purple	Green	Green
95	Darker but not green		Purple → black → green	

$$3MnO_4^{=} + 2H_2O \longrightarrow 2MnO_4^- + MnO_2 + 4OH^{-\,9} \qquad (2)$$

A third aliquot of the hot 12.4 N potassium hydroxide final mixture was heated with a concentrated solution of potassium hydroxide and rapidly cooled; a fourth portion was treated with the concentrated alkali and evaporated isothermally at 95'—neither procedure giving uniform results, even on repetition. In a few cases a crystalline product separated out from the cooled samples, whereas a mixture of manganese dioxide and a crystalline substance usually separated from the evaporated sample. The crystalline product from both procedures was of a dark green color and had the following crystallographic properties.

The crystals were imperfect rhombohedrons, pseudo hexagonal, striated vertically, almost opaque, showed no pleochroism and no color change under the Nicol prism of the polarizing microscope. They were always contaminated with manganese dioxide and alkali, and usually permanganate crystals could also be detected. Purification of them was difficult as a drop of water would give a dark green solution which upon dilution turned pink with the precipitation of manganese dioxide

These crystallographic data show these crystals to be identical with potassium manganate.[10] Gorgeu[11] by a slightly different procedure obtained the double salt $KMnO_4 \cdot K_2MnO_4$ crystallizing in the monoclinic system. The above experimental data, however, warrant the conclusion that potassium manganate and not a double salt is the product of the reaction.

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[9] *Cf.* (a) Dieffenbach, German Patent 195,523 (1867), and (b) Ruby, THIS JOURNAL, 43,294 (1921).

[10] (a) Mitscherlich, *Pogg. Ann.*, 25, 287 (1832); (b) Retgers, *Z. physik. Chem.*, *8*, 6 (1891).

[11] Gorgeu, *Compt.* rend., 110, 1134 (1890).

The color changes for the corresponding sodium permanganate–sodium hydroxide reactions are given in Table III. Most of the efforts to obtain a crystalline product from the 6.62 and 11.51 *N* sodium hydroxide series at 95° were unsuccessful, as the crystals generally disappeared or decomposed in the course of their isolation and purification. If a little water or dilute alkali was brought in contact with them a dark green mass resulted which upon being dried was found to be mainly manganese dioxide. The few which were secured were so contaminated with alkali that it was impossible to purify them for crystallographic analysis. Finally, by allowing a dark green reaction mixture to stand for twenty-four hours after treatment with concentrated sodium hydroxide, and then cooling somewhat, a good crop of well-formed dark green (almost black) crystals was obtained. A few of these upon treatment with a drop or two of water gave a dark green solution and on further dilution gradually turned pink. The remainder was dried by a short contact with blotting paper and then over sulfuric acid, and examined under the polarizing microscope.

TABLE III

COLOR CHANGES

Temp., °C.	Alkalinity			
	3.12 N	4.05 *N*	6.62 N	11.51 N
50	Purple	Purple	Dark purple	Greenish
75	Purple	Purple	Green	Greenish
95	Purple	Dark purple	Greenish	Green

They consisted of orthorhombic prisms striated vertically with cleavage parallel to the side pinacoid and gave a very dark purple color upon fresh fracture which quickly tarnished to a brown. The crystals rapidly decomposed in the air. Their color was so dark that no interference figures were observable with polarized light.

These crystals may have been either sodium manganate or the hydrated form.[12] The evidence favors some form of sodium manganate as a product of the reaction between sodium permanganate and sodium hydroxide.

At 95° with both the potassium and sodium series of reactions, a gas (identified as oxygen) was very slowly but visibly given off. There was no visible gaseous evolution in the 50 and 75° series.

The available oxygen titer is a measure of either the permanganate or manganate ions, hence any intermediate titer does not give the measure of either ion when both are present. Obviously then no conclusive calculations of the velocity constants are possible. For indicative purposes only, the authors calculated the approximate velocity constants using the commonly accepted integrated equations for first- and second-order reactions and also the differential equation

$$-\frac{d(MnO_4^-)}{dt} = 4\frac{d(O_2)}{dt} = K_2(MnO_4^-)^2 \qquad (3)$$

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[12] Auger, *Compt. rend.*, 151, 69 (1910).

for a second order reaction and found that these values favored a reaction of the second order with respect to MnO_4^-.

These approximate constants also tend to support the intermediate formation of an hydrated ion as indicated in the equation

$$MnO_4^- + 4OH^- \longrightarrow MnO_4^- \cdot 4OH^- \longrightarrow MnO_4^= + 2H_2O + O_2 \qquad (4)$$

For example, in the 95° $KMnO_4$–KOH series, the constants (from the integrated bimolecular equation) for the alkalinities 5.65, 7.09, 9.52 and 12.4 N were substantially the same at 48, 96, 144 and 240 hours, respectively.

Jolles[13] prepared potassium manganate in accordance with Equation 1 and reported theoretical yields by using concentrated solutions of alkali and permanganate. Kassner and Keller[14] obtained a green solution but were unable to isolate any of the manganate. Without question, manganese dioxide is formed from the permanganate when reducing agents (particularly organic) are present. In the present investigation no microscopic evidence was found showing the formation of either precipitated or colloidal manganese dioxide. If it was a reaction product, it was present in less than colloidal dimensions or else was consumed in a subsequent or simultaneous reaction. Equation 1 then is substantiated in so far as the dioxide is concerned. Sackur and Taegener[15] found that Equation 1 was not reversed by the addition of atmospheric oxygen. No one has reported the study of the effect of atomic oxygen or ozone. If the non-reversibility of Equation 1 is accepted, then an equilibrium condition in the reactions reported herein cannot be considered. The method used by the authors in estimating the available oxygen is based on

$$4MnO_4^- + 12H^+ \longrightarrow 4Mn^{++} + 6H_2O + 5O_2 \qquad (5)$$

If the reaction indicated in Equation 1 proceeded to completion, only one-fifth of the total available oxygen in a reaction mixture would have been evolved. The initial titer of all of the potassium permanganate reaction mixtures was 0.156 mole of available oxygen. The maximum loss of available oxygen, then, on the basis of Equation 1, would be 0.0312 mole and the lowest possible solution titer would be 0.1248 (0.068, for the $NaMnO_4$ series) mole of oxygen. With the exception of the experiment involving the permanganate and 12.4 N hydroxide (see broken line in Fig. 4 and also Table IV) the oxygen titer in the potassium ion experiments was above 0.1248 mole. In this one exception the oxygen value did not become constant until it reached 0.101 mole or there was an oxygen loss of 35.2%, which is 15.2% more than is required by Equation 1. This extra loss might seem a substantiation of the equation

$$4MnO_4^- + 2H_2O \longrightarrow 4MnO_2 + 4OH^- + 3O_2 \qquad (6)$$

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[13] Jolles, Z. *Naturw.*, [4] *5,423* (1886).

[14] Kassner and Keller, ***Arch. Pharm.,239,473*** (1901).

[15] Sackur and Taegener, Z. ***Elektrochem.,*** 18,718 (1912).

of Sackur and Taegener. Smith[16] assumed the formation of a peroxide from the oxygen which remained in solution. While this or a similar possibility has not been proved, an analogous compound $H_2O_2 \cdot K_2CrO_4$[17] has been isolated. Maksimov,[18] upon dissolving the potassium or sodium permanganate in solutions of their respective hydroxides, obtained the dioxide and oxygen and postulated the presence of the alkali peroxide in the resulting solution. As evolved oxygen was not detected in the reaction mixtures of lower alkalinity in this investigation, it is possible that a portion or all of the oxygen set free in the major reaction may have been consumed in the formation of an alkali peroxide. This, however, is not in harmony with our knowledge of the interactions of alkali peroxides and water. It is more likely that the oxygen was in solution for those reactions at the lower temperatures. For the $NaMnO_4$–$NaOH$ series of reactions the highest percentage loss of available oxygen for each of the temperatures (50, 75 and 95°) was 8.2, 17.6 and 23.5%, respectively.

One gram of manganese dioxide dried at 100° was added to a reaction flask containing 200 cc. of 12.4 N potassium hydroxide and 200 cc. of the potassium permanganate and the reaction allowed to proceed at 95°. The contrast in behavior between this mixture and another containing none of the dioxide is given in Table IV. At about seventy-two hours the reaction mixture turned brown in color and further analysis by the procedure previously used became impossible. The manganese dioxide not only increased the speed of the reaction but also brought about complete decomposition. A second experiment in which was used manganese dioxide from another source gave widely different results, except that the rate of decomposition was not apparently changed for the first twenty-four hours, but at the end of this time the brown decomposition resulted as before. These observations with added manganese dioxide confirm

TABLE IV

EXPERIMENTAL DATA

Time, hours	Available oxygen, mole per liter No MnO_2	 1 g. MnO_2 (hydrated)
0	0.156	0.156
4	.146	.137
24	.133	.128
48	.120	.109
72	.116	
140	.106	
240	.101	
320	.101	

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[16] Smith, *J. Soc. Chem. Ind.*, **6**, 260 (1887).

[17] Moissan, *Traité Chim. Min.*, 1, 275 (1904).

[18] Maksimov, *J. Russ. Phys.-Chem. Soc.*, **57**, 357 (1925).

in a general way the work of Brand and Ramsbottom,[19] although these investigators do not mention total decomposition as having taken place. The previous history then of the dioxide is of importance in this reaction.

The oxides of manganese are good adsorbents of both alkali metal and hydroxyl ions. The gel form of manganese dioxide has been prepared, which suggests that the hydrated sol form may also exist. Hydrated ferric oxide sol is not visible under the ultramicroscope and this invisibility may also hold for the possible hydrated manganese dioxide sol. The dioxide may also have been present as a true solution in the highly alkaline media used in this investigation. The final conclusion is that neither the colloidal nor the precipitated form of manganese dioxide was a reaction product of the reactions recorded in Fig. 2 for the reasons that: (a) the oxygen loss ceased beyond a certain time; (b) manganate was present in the final solutions (see Tables II and III); and (c) added colloidal and precipitated manganese dioxide caused the complete disappearance of the permanganate and manganate from the reactions studied in this and other investigations.

Gorgeu[20] obtained the double salt $KMnO_4 \cdot K_2MnO_4$ [or $(K_{1.5}MnO_4)_2$] from an alkaline solution of the two salts, which was soluble in a 20% potassium hydroxide solution without decomposition. Potassium mangani-manganate having the formula $5K_2O \cdot Mn_5O_{13}$ [or $(K_2MnO_{3.6})_5$] and sodium mangani-manganate having the formula $4Na_2O \cdot Mn_2O_5$ [or $(Na_4MnO_{4.5})_2$], have been described by Sackur[21] and also by Auger.[22] Morawsky and Stingl[23] found potassium in combination with the hydrated oxide or oxides of manganese and assigned to this the formula $Mn_4KH_3O_{10}$ [or $(K_{0.25}MnO_{2.125})_8 \cdot (H_2O)_3$]. In view of the above facts it seems likely that a more or less continuous series of (a) double salts, or (b) double oxides of the alkali metal and manganese existed in the reaction mixtures described in this paper. The identification of the hydrated manganates and not other manganese compounds is still unexplained.

Manganese Dioxide.—The character of the' manganese dioxide obtained and observed during these experiments is of interest. A suspension of manganese dioxide formed when a dark green reaction mixture, consisting probably of potassium permanganate, manganate, water and potassium hydroxide, was diluted. The color of this dioxide was almost jet black when wet, which slowly changed to a dark brown upon being washed and dried at 100°. The oxide obtained from different dilutions of the reaction mixture likewise varied in color—brownish-black to light

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[19] Brand and Ramsbottom, *J. prakt. Chem.*, [2] *82*, *366* (1910).

[20] Gorgeu, *Compt. rend.*, 110, 958 (1890).

[21] Sackur, *Ber.*, **43,** 381 and 448 (1910); ibid., 44, 777 (1911).

[22] Auger, *Compt. rend.*, 150, 470 (1910); *ibid.*, **151,** 69 (1910).

[23] Morawsky and Stingl, J. *prakt. Chem.*, [2] 18, 82–83 (1878).

brown—as did the samples obtained from the permanganates of sodium and potassium. One of the authors[24] observed this same sort of color variation when working with alkaline permanganate solutions in the presence of organic reducing agents.

When a 400-cc. dark green alkaline reaction mixture of sodium permanganate and sodium hydroxide was diluted with 100 cc. of distilled water and evaporated over an open flame, a point was reached where a jelly-like precipitate of manganese dioxide was formed. This form and its conversion into a hydro-sol has been described by Witzemann.[25] His procedure for obtaining it varied from the above in that he reduced an alkaline permanganate solution with glucose and other organic material. The jelly obtained in the present investigation when diluted with water and dried at 100° formed a hard wax-like cake, which had a resinous luster upon fresh fracture. Inorganic jellies of this type have been described by Weiser[26] in a comprehensive review, but no mention is made of the jelly form of manganese dioxide. This jelly was quite stable in alkaline solution, but upon dilution changed into the suspensoid form.

Summary

1. Aqueous solutions of potassium and sodium hydroxides were prepared which when acidified with sulfuric acid did not reduce a dilute solution of potassium permanganate.

2. Aqueous solutions of potassium and sodium permanganate were prepared which were free from both precipitate and colloidal-size particles of the oxides of manganese.

3. Studies of the reactions between these permanganates and their corresponding hydroxides at 50, 75 and 95° show that *(a)* the reactions are very slow; *(h)* an increase in temperature increases the speed of the reactions with progressive lowering of the available oxygen; (c) beyond a certain minimal concentration of alkali an increase in the alkalinity progressively lowers the available oxygen to constancy with time; (d) potassium manganate and oxygen and sodium manganate and oxygen were isolated and identified as reaction products in their respective reaction series; (e) manganese dioxide either in precipitated or colloidal state was not isolated or identified in these reactions: (f) both series of reactions are probably bimolecular and the equation

$$4MnO_4^{-} + 4OH^{-} \longrightarrow 4MnO_4^{=} + 2H_2O + O_2$$

satisfactorily accounts for the reactions at 50 and 75° but not at 95°; (g) at 95° the reaction mixtures for both the Na^+ and K^+ series lost more

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[24] J. E. Day, "Dissertation," The Ohio State University, 1919.

[25] Witzemann, THIS JOURNAL, 37, 1079 (1915).

[26] Weiser, "Colloid Symposium Monograph," University of Wisconsin, pp. **38–62** **(1923).**

available oxygen than is demanded by the equation in (f); and *(h)* the results obtained are best explained on the assumption that a continuous series of double salts of manganese or double oxides of the alkali metal and manganese were formed in the strongly alkaline solutions.

4. The initial presence of precipitated manganese dioxide in a reaction mixture brings about an ultimate decomposition of the perrnanganate to the dioxide in a relatively short time when compared with the time for the reactions summarized in **3** *(a)*.

5. Slow stirring of a reaction mixture increases the speed slightly without appreciably influencing the point of apparent rest in the reaction.

6. A new method for the preparation of manganese dioxide gel is described.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ELECTROMOTIVE ACTIVATION OF OXYGEN

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RECEIVED DECEMBER 1, 1930 PUBLISHED JANUARY 12, 1931

The achievement of a fuel cell, in which the free energy of combination of hydrogen or some comparable gaseous fuel with oxygen is converted directly into electric energy, has encountered its most serious difficulties at the oxygen electrode. Gaseous oxygen establishes its potential sluggishly and imperfectly on inert electrodes at ordinary temperatures, even on open circuit, and an oxygen electrode on closed circuit polarizes at once if any appreciable current is withdrawn.

These difficulties have been overcome to some extent by operating the electrodes in suitable electrolytes at elevated temperatures.[1] Similarly progress has been made in the electromotive activation of oxygen by the use of catalysts. These catalysts have been of two types. In the one type, the catalytic action is confined to the surface of the electrode, the catalyst being either a part of the electrode itself or a reaction product formed upon its surface, which enhances the electromotive activity of the gaseous oxygen. Electrodes where catalysts of this type are effective are the familiar platinized platinum and similar electrodes, and the electrode of copper immersed in a solution of potassium hydroxide described by K. A. Hofmann.[2] In the second type the catalytic action takes place throughout the bulk of the electrolyte. This type of catalyst must be susceptible of rapid oxidation by gaseous oxygen under the conditions in the cell, and its oxidation product must be a rapid depolarizer.

[1] Haber and Bruner, Z. *Elektrochem.*, 10, 712 (1904); Taitelbaum, *ibid.*, 16, 286 (1910); Baur, Treadwell and Trümpler, *ibid.*, 27, 199 (1921); *Helv. Chim. Acta*, 4, 325 (1921); Rideal and Evans, *Trans. Favaday Soc.*, 17,466 (1921).

[2] Hofmann, *Ber.*, 51,1526 (1918); 52,1185 (1919); 53,914 (1920).

This second type of catalyst, or bulk catalyst, as one may call it, has the marked advantage over the first type, or surface catalyst, in that with it the chemical oxidation of the catalyst by the gaseous oxygen, which in general is a relatively slow step in the process as a whole, can take place far more abundantly, and with adequate stirring the oxidized catalyst can be brought into effective contact with the electrode. Nernst[3] patented this method some time ago, and suggested a variety of catalysts for its execution, but apparently it has not as yet been put into successful operation. Nevertheless, the method has seemed to us to be of considerable promise, and the experiments which we shall describe below have been directed toward its further development.

The catalyst to be used in such a method of overcoming the easy polarizability of the oxygen electrode should meet several requirements. As pointed out above, it should be susceptible of rapid oxidation by gaseous oxygen under the conditions in the cell, and its oxidation product should be a rapid depolarizer. But it is also desirable that the normal potential of the catalyst system approximate that of the reversible oxygen electrode in the electrolyte used. Other things being equal, this will afford the highest working potential for the electrode.

There are a number of catalyst systems which give rapidly adjusting and reversible potentials, but unfortunately they absorb oxygen very slowly. Conversely, there are several such systems which absorb oxygen rapidly, but their potentials are very low. Examples of the former group are the thallous–thallic and vanadyl–vanadic acid systems; of the latter are the vanadous–vanadic and the chromous–chromic systems. The ferrous–ferric system occupies a somewhat favorable intermediate position; it establishes its potential with great rapidity on various electrodes; it has a fairly high normal potential; but it reacts with gaseous oxygen with only slight (though measurable) rapidity. However, the kinetics of this reaction have been studied to some extent, and a variety of factors which increase its velocity, particularly secondary catalysts, such as copper salts, platinum black and charcoal, have been recognized.

We have, therefore, undertaken a further study of the velocity of oxidation of ferrous solutions by gaseous oxygen, since this is the limiting factor in the utility of the ferrous–ferric system as a bulk catalyst. For this study we have perfected a method of determining the rate of oxidation of ferrous solutions by means of electromotive force measurements. Using this method we have ascertained the effects of a variety of factors on the velocity of the reaction. Finally, we have tested the actual depolarizing efficiency of certain of the systems which had shown the maximum velocity of reaction with gaseous oxygen.

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[3] Nernst, *German* Patents 260,426 *and* 265,424 (1912). See also Grube and Hermann, *Z. Elektrochem.*, 26,291 (1920).

Procedure and Apparatus

Velocity of Oxidation of Ferrous Sulfate Solutions by Gaseous Oxygen.—Oxygen in air was bubbled through the solution to be studied and the progress of the oxidation was followed by measurements of the potential of a bright platinum electrode immersed in the solution.

The apparatus (see Fig. 1), constructed chiefly of pyrex glass, comprised a short, wide test-tube **(A)** containing the solution of iron salt (50.2 cc.); a tubular stirrer (S), with four slightly re-curved tips (C) at its base at right angles to its axis; a baffle (D) to prevent undue swirling of the liquid; an electrode (K); and a saturated potassium chloride bridge (F), connecting the ferrous salt solution with *a* reservoir (H), filled also with saturated potassium chloride solution and connected in turn with the tip (N) of the calomel electrode. The whole was immersed to within a few millimeters of its top in a thermostat bath (P) maintained at a temperature of 30.0 ± 0.1°.

The stirrer was rotated by means of an induction motor at constant speed and rapidly enough to force air through the solution in a fine, white foam. The standard rate of stirring was 1250 r. p. m.

The electrode was of bright platinum wire 2–3 cm. in length. It and the salt bridge (F) were lowered into the solution only at the time of reading. When not in use it was kept short-circuited with several duplicate electrodes in a ferrous–ferric salt mixture, and was washed and ignited to a red heat before each run. In this way constant and reproducible potentials could be secured. Preliminary measurements showed that the potential of the electrode in any given solution was independent of the presence of the gaseous oxygen.

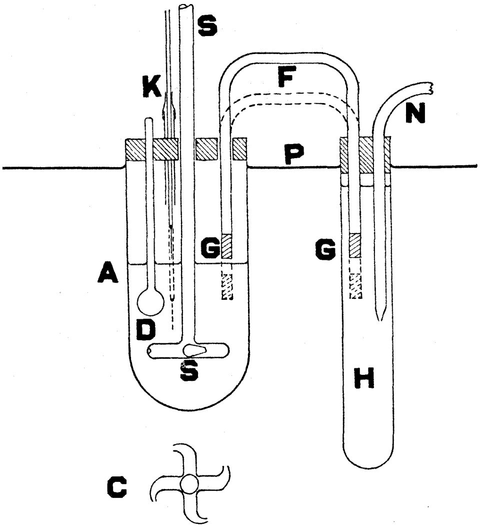

Fig. 1.—Apparatus for kinetic measurements.

The calomel electrode was of the saturated type prepared according to the method of Fales and Mudge,[4] using all the customary precautions in purifying the materials. Three such electrodes were prepared. Their potentials checked against each other from time to time showed an average agreement to within ±0.0005 v. Fales and Mudge give the absolute potential of this electrode as $E_0 = 0.5266$ v., which corresponds to E_h

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[4] Fales and Mudge, This journal, 42, **2453** (1920).

$= +0.253$ v. on the hydrogen scale. The potentiometer was of the compensating type, using an Eppley–Weston standard cell.

Materials.—The ferrous sulfate used was recrystallized from one to two per cent. sulfuric acid and dried to incipient efflorescence in air. Prepared in this way we found that it could be kept for months without appreciable oxidation. The solutions were made up by weight from the above material, and their composition checked by analysis. Ferrous iron was determined in the usual manner by titration with potassium permanganate. Ferric iron was titrated in partially oxidized solutions containing 0.005 to 0.01 N Fe^{+++} by iodimetry under carbon dioxide, using specially prepared reagents.[5] The initial ferric-ion concentration of the "unoxidized" stock solution was calculated from this by applying Equation 3 (see below) to the corresponding potentials. This equation holds fairly accurately over this small range at such low concentrations. For subsequent runs it was only necessary to weigh out a sample of equal weight to make the same volume of solution and compare its initial potential with that of the calibration, as outlined above.

Computation of the Progress of the Oxidation from the Potentials.—We had hoped to be able to compute the progress of the oxidation directly from the observed change in potential AE, since

$$\Delta E = \frac{RT}{F}\ln\left[\frac{\gamma_2{}^{+++}\,\mathrm{Fe_2}{}^{+++}}{\gamma_1{}^{+++}\,\mathrm{Fe_1}{}^{+++}} \times \frac{\gamma_1{}^{++}\,\mathrm{Fe_1}{}^{++}}{\gamma_2{}^{++}\,\mathrm{Fe_2}{}^{++}}\right] \tag{1}$$

where γ^{++} and γ^{+++} represent the activity coefficients of the ferrous and ferric ions and the subscripts 1 and 2 refer to the initial and final concentrations, respectively. This equation becomes

$$AE = \frac{RT}{F}\ln\left[\frac{(\mathrm{Fe_1}{}^{+++} + AC)}{\mathrm{Fe_1}{}^{+++}} \times \frac{\mathrm{Fe_1}{}^{++}}{(\mathrm{Fe_1}{}^{++} - \Delta C)}\right] + \frac{RT}{F}\ln\left[\frac{\gamma_2{}^{+++}\,\gamma_1{}^{++}}{\gamma_1{}^{+++}\,\gamma_2{}^{++}}\right] \tag{2}$$

where AC represents the change in the concentration of the ferric ion corresponding to the change in potential AE.

From Equation 2 it is clear that to compute AC in this way for any value of Fe^{++} and Fe^{+++} we must know, in addition to AE, either the activity coefficients of the ferrous and ferric ions under the conditions of our experiments (which unfortunately we do not), or we must be able to consider the last term on the right of the equation as equal to zero. In this case Equation 2 can easily be rewritten as

$$\Delta C = \mathrm{Fe_1}{}^{+++}\,\mathrm{Fe_1}{}^{++}\left[\frac{e^{(F\Delta E/RT)} - 1}{\mathrm{Fe_1}{}^{++} + \mathrm{Fe_1}{}^{+++}e^{F\Delta E/RT}}\right] \tag{3}$$

which gives AC directly in terms of known or measured quantities.

We have conducted numerous experiments to test this latter alternative, measuring the changes of potential produced by the addition of known amounts of potassium permanganate to solutions of ferrous sulfate. Corrections were applied for the disturbing effects of the reaction

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[5] Morse and Burton, Am. *Chem.* J., 10, 321 (1888).

products from the potassium permanganate which will be explained later in another connection. We found that the change in concentration of the ferric ion could be calculated accurately by means of the simplified Equation **3** only when the concentrations lay within certain narrow limits, namely, when the ferric ion was less than about 0.001 *M* and the sulfuric acid was between 1.0 *M* and 0.01 M. When the concentrations departed from these limits, the divergence of the observed potentials from the calculated values became considerable and in extreme cases the discrepancy was as much as 500%. This is shown by the typical results collected in Table I.

TABLE I

COMPARISON OF CALCULATED AND ACTUAL CONCENTRATIONS

Solution, m. mol.	ΔE obs. (corr.), mv.	ΔC Calcd. from ΔE, m. mol.	ΔC Actual from $KMnO_4$, m. mol.	Solution m. mol.	ΔE obs. (corr.), mv.	ΔC Calcd. from ΔE, m. mol.	ΔC Actual from $KMnO_4$, m. mol.
$Fe^{+++} = 0.405$ $Fe_2SO_4 = 183$ $H_2SO_4 = 11.0$	33.0	1.03	0.98	$Fe^{+++} = 0.172$ $FeSO_4 = 150$ $H_2SO_4 = 3000$	32.5	0.422	1.94
	46.0	1.94	1.95		46.7	.855	3.87
	54.8	2.87	2.93		54.1	1.18	5.80
	60.3	3.61	3.90		62.2	1.68	7.74
$Fe^{+++} = 3.98$ $FeSO_4 = 178$ $H_2SO_4 = 12.0$	5.4	0.90	0.98	$Fe^{+++} = 5.35$ $FeSO_4 = 131$ $H_2SO_4 = 500$	3.9	0.82	0.84
	10.1	1.83	1.95		4.5	.95	.98
	12.8	2.44	2.93		4.6	.98	1.00
	15.3	3.05	3.90		8.1	1.82	1.84

The explanation of these discrepancies probably is that at high concentrations of sulfuric acid or of ferric ions the activity coefficients are markedly different from unity; at low concentrations of sulfuric acid, on the other hand, the hydrolysis of the ferric salt becomes of importance. Whatever the explanation, it is clear that this direct method of computation cannot be used successfully.

Failing then an accurate method of calculating the amount of oxidation from the corresponding potential change, resort was taken to a purely empirical method of calibration. Blank experiments were run in the solutions whose rates of oxidation were to be measured, where a known amount of oxidation was secured by the addition of measured quantities of potassium permanganate. The observed potential changes thus obtained were then corrected for the dilution produced by the introduction of the permanganate solution and for the effect of the potassium and manganous ions. These correction terms were ascertained by adding to a control solution equal volumes of a solution of potassium and manganous sulfates to approximately the same concentration as that resulting from the reduction of the standard potassium permanganate. The resulting potential change is the desired correction term. This procedure affords a measure of the change in potential due solely to the introduction of oxygen.

The following data for a particular solution will serve as an illustration (Table II).

TABLE II

CALIBRATION DATA FOR $FeSO_4$ 0.148 M; H_2SO_4 1.0 M

Initial $E_C = +0.3614$

$KMnO_4$, 0.002528 N, cc.	ΔC equiv. concn. of oxygen per liter of original $FeSO_4$	AE observed, mv.	Correction term. mv.	AE corrected, mv.
9.85	0.000495	13.8	− 1.5	15.3
19.70	.000991	22.9	− 3.7	26.6
29.55	.001487	30.1	− 8.5	38.6
39.40	.001982	36.3	− 9.5	45.8

The corrected values of AE were plotted against the corresponding values of AC and the resulting curve served as a calibration curve (Fig. 2). In using it, the initial potential of the system being observed was compared with the initial potential of the calibration curve and the value of AC corresponding to this difference was subtracted from each subsequent value of AC read from the curve. In other words, the curve applied to each run was referred to the initial potential of that run as origin. An example follows, using the calibration data given above.

TABLE III

RUN NO. 325

DATA

$\left[\begin{array}{ll} H_2SO_4 & 1.0\ M \\ FeSO_4 & 0.15\ M \end{array}\right|$ Saturated KCl $\Big|$ Calomel$\Big]$

Without aeration		With aeration	
t	E_C	t	E_C
3.45 P. M.	+0.3614	7.35 P. M.	+0.3712
		8.52	+ .3737
		9.39	+ .3756
		9.20 A. M.	+ .3896
		10.47	+ .3920

TABLE IV

CALCULATION

t, hrs.	ΔE (E_C − 0.3814) mv.	AC from curve m. mol.	ΔC (from initial t) m. mol.	2d order constant, $K_2 \times 10^5$
...	9.8	0.000320	.....	...
1.28	12.3	.000405	0.000085	295
2.07	14.1	.000465	.000145	311
13.75	28.2	.001030	.000710	230
15.20	30.6	.001130	.000810	237
(AC = 0.000810 ≈ 0.22 cc. O_2 at N. T. P.)			Av. =	268 ± 35

In order to facilitate comparison of the velocities under varying conditions, we have computed velocity constants from corresponding values of t and AC, both assuming a first- and a second-order reaction. In most cases reasonably constant values (average deviation from the mean = ±10%) were obtained on *both* assumptions. This result is readily understood when it is appreciated that in most of our experiments only about one per cent. of the ferrous salt present was oxidized, so that experimental and other variations would mask the relatively small differences in the trend of the constants calculated on the two different assumptions. In a later section experiments to ascertain more definitely the order of the reaction are described. Since our aim here was primarily to secure a means of comparison, we have, in general, used the constant for a second order reaction

$$K_2 = 1/t \frac{\Delta C}{\text{Fe}_1^{++}(\text{Fe}_1^{++} - \Delta C)}$$

as easier to compute arithmetically. Occasionally the velocity measurements have given constants with a drift or trend, sometimes in the one direction and sometimes in the other, for no assignable reason. Duplicate measurements have often eliminated this uncertainty, so that it has apparently been due to some accidental effect. Where such drifting constants have been obtained, the average value is relatively uncertain and we have indicated this by enclosing such values in parentheses.

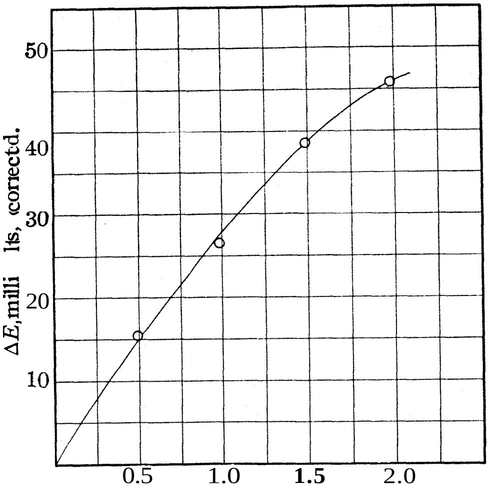

Fig. 2.—Calibration **curve.**

The usual average deviation of the constants in any one run was, as stated above, ±10%. The usual reproducibility of our results for a given solution is shown, for instance, by the average values of the constant (K_2) obtained in seven duplicate runs on the solution $FeSO_4$ 0.169 *M*, H_2SO_4 0.50 *M*, as follows: 313, 338, 265, 263, 307, 261, 259 X 10^{-5}; grand average 287 × 10^{-5} ± 9%.

Experimental Results

Effect of Variations in the Rate of Stirring.—The normal rate of stirring, as pointed out above, was 1250 r. p. m. Although the "atomization" of the injected air was excellent, it was necessary to find out whether the observed rate of oxidation was limited by the rate of solution of the oxygen, or by the rate of reaction of the dissolved oxygen. To accomplish this we have varied the rate of stirring under various conditions over relatively wide ranges. The results are shown in the following table (Table V) where the average values of the constants obtained in the various runs are recorded, computed on the assumption of a second-order reaction.

TABLE V

EFFECT OF RATE OF STIRRING ON VELOCITY OF REACTION

$FeSO_4$ 0.15 *M*; H_2SO_4 1.0 *M*;				$FeSO_4$ 0.15 *M*; H_2SO_4 0.5 *M*; 1 g. of charcoal per 50 cc.			$FeSO_4$ 0.15 M; H_2SO_4 1.0 M 10 g. of charcoal per 50 cc.		
	Kz × 10^5				K_2 × 10^5			K_2 × 10^5	
Expt.	720 r. p. m.	1250 r. p. m.	1640 r. p. m.	Expt.	1250 r. p. m.	1640 r. p. m.	Expt.	1250 r. p. m.	1920 r. p. m.
1	290	253	349	1	81300	75000	1	305000	713000
2	271	289	268	2	65400	84100	2	311000	408000
3	...	295	267	3	79500	...		...	...
4	...	(309)	...	4	67500	...			
5	...	(211)	...	5	66400	...			
	...	...	...	6	66900	...		...	...
Mean	280	279	295	Mean	71200	79500	Mean	308000	560000
K_2 at 1250 r.p.m. = 6.36 × 10^{-5} eq. of O_2 per liter per hr.				K_2 at 1250 r. p. m. = 0.0115 eq. of O_2 per liter per hr.			K_2 at 1250 r. p. m. = 0.0328 eq. of O_2 per liter per hr.		

It is obvious from the above results that only those reactions which proceed at a rate greater than about 0.0115 equivalent of O_2 per liter per hour, corresponding to a second-order constant K_2 of about 0.7 (i.e., 70,000 × 10^{-5}), are affected appreciably by the rate of stirring at a rate of 1250 r. p. m.

Effect of the Variation of Concentration of the Oxygen.—The times required for 0.5% oxidation by means of air and pure (commercial) oxygen, in different portions of the same solution, are given in the following table (Table VI).

TABLE VI

EFFECT OF THE CONCENTRATION OF THE OXYGEN

Times to 0.5% oxidation: $FeSO_4$ 0.15 M; H_2SO_4 0.50 M

Expt.	Air, hrs.	Oxygen, hrs.
1	14.5	3.10
2	14.4	2.50
3	10.3	..
4	11.2	..
5	13	..
	12.7 ± 1.6	2.80 ± 0.3

The ratio of the times is 1:4.54, or substantially what would be expected (1:5.0) on the assumption that the reaction is unimolecular with respect to the oxygen.

Effect of Variation in the Concentration of the Ferrous Sulfate.—As pointed out above, the percentage oxidation of the ferrous sulfate in these experiments was relatively so inconsiderable that the constancy of any particular "velocity constant" based on a single initial concentration affords no certain evidence as to the order of the reaction with respect to the ferrous sulfate. To obtain more conclusive evidence on this point we have carried out two sets of comparative experiments where there were marked differences in the initial concentration of the ferrous sulfate, and have compared the times required to produce 1% oxidation. The data are presented in Table VII.

TABLE VII

EFFECT OF THE CONCENTRATION OF FERROUS SULFATE

Time in hours for 1% oxidation

	Set 1		Set 2	
Expt.	$FeSO_4$ 0.169 M $HeSO_4$ 0.23 *M*	$FeSO_4$ 1.36 M H_2SO_4 0.18 *M*	$FeSO_4$ 0.170 M H_2SO_4 2.0 M	$FeSO_4$ 1.24 M H_2SO_4 2.0 *M*
1	21.2	4.52	30.5	4.31
2	(16.7)	4.09	25.6	4.32
3	22.1	..		
4	25.2	..	..	..
5	22.9	..	..	..
Mean	22.8 ± 1.2	4.31 ± 0.2	28.1 ± 2.6	4.32 ± 0.01

Ratio of total ferrous concentrations........... 1:8.0....................... 1:7.3

Ratio of velocities............1:5.3.......................1:6.5

One can see from the above results that the initial velocities are approximately proportional to total ferrous salt concentrations in the two pairs of comparable solutions. This indicates, since the oxygen concentration was kept constant throughout the runs, that the reaction is approximately bimolecular with respect to the ferrous salt. The deviations are about what one would expect if the velocity were directly proportional to the activity of the ferrous ion rather than to the total ferrous salt concentration, but the data are hardly accurate enough to justify any numerical calculation.

Effect of Variation in the Concentration of the Acid.—The data obtained bearing on this point are collected in Table VIII.

TABLE VIII

EFFECT OF VARIATION IN THE CONCENTRATION OF THE ACID

$FeSO_4$ *M* H_2SO_4 *M*	0.146 0.008	0.176 0.012	0.146 0.055	0.169 0.23	0.17 0.50	0.181 1.0	0.170 2.0	0.15 3.0
Expt.	$K_2 \times 10^5$							
1	(1280)	528	453	289	338	253	(213)	294
2	(1250)	580	377	357	265	289	(245)	234
3	..	...	...	281	263	295	...	
4	..	...	...	236	307	...	...	
5	..	...	...	269	261	...	...	...
Mean	(1265)	554	415	286	287	279	(229)	264

These mean values of K_2 are also plotted in Fig. 3. It is evident that change of acid concentration between the limits of 3.0 M and 0.23 M produces scarcely any change in reaction velocity; indeed, the change is scarcely beyond the limits of error. A decrease in acid concentration below 0.23 M, however, increases the velocity, the rate of increase rising rapidly as the acid becomes more dilute. This relation is in accord with the fact that acid solutions of ferrous sulfate are relatively stable in air, whereas ferrous hydroxide absorbs oxygen from air with great rapidity.

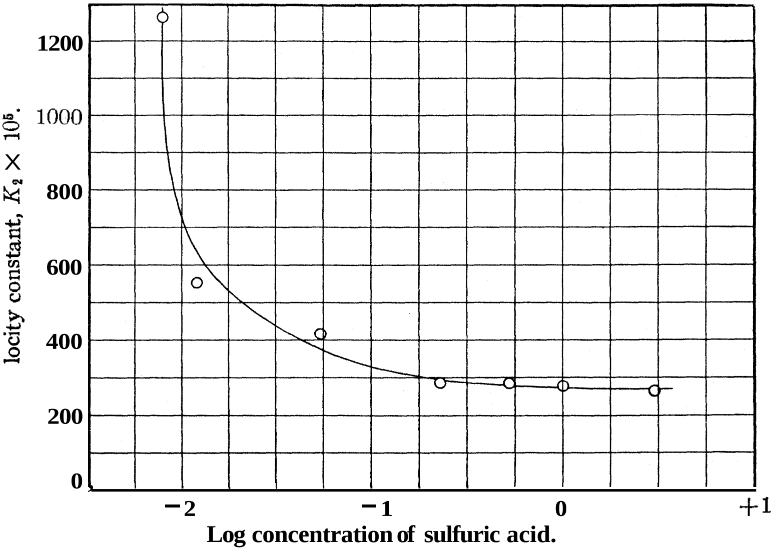

Fig. 3.—Variation of the velocity with the concentration of the sulfuric acid. $FeSO_4$, 0.15–0.18 M.

Effect of Neutral Salts.—Sufficient of each of a variety of salts was added to portions of a stock solution to be 0.1 M. The velocity constants obtained are collected in Table IX.

TABLE IX

EFFECT OF SALTS

$FeSO_4$ 0.15 M; H_2SO_4 0.52 M

Salt / Expt.	Na_2SO_4	K_2SO_4[a]	$MgSO_4$[a]	$ZnSO_4$	$MnSO_4$	$Cr_2(SO_4)_3$	NaAc	Na_3PO_4	$NiSO_4$[a]	None
	$K_2 \times 10^5$									
1	300	240	357	239	301	192	266	290	340	
2	263	221	290	423	213	195	295	286	381	
3	372	291	...	...	...	...	283	...	...	
Mean	312	251	323	331	257	194	281	288	360	287

[a] These solutions contained 0.23 M H_2SO_4.

Similar experiments were made with Ag_2SO_4 0.1 M and Hg_2SO_4 0.001 M, and except for the fact that they were in whole or in part reduced by the ferrous sulfate, the results were substantially identical with those obtained with the solutions already cited.

It follows from the data that these salts are practically without effect on the velocity of oxidation of the ferrous sulfate by the gaseous oxygen.[6]

The Effect of Copper Sulfate.—It has long been known that copper salts accelerate the oxidation of ferrous salt solutions by oxidizing agents[7] and by gaseous oxygen.[8] The results of our measurements are given in Table X.

TABLE X

EFFECT OF COPPER SULFATE

$FeSO_4$ M	0 16	0.170	0.171	0.16	0.169	0.161	0.176
H_2SO_4 M	3.0	2.0	1.0	.52	.23	.055	.012
$CuSO_4$ M	0.1	0.1	0.1	.1	.1	.1	.1
Expt.	$K_2 \times 10^5$						
1	38700	(18860)	20242	13265	(8810)	(5087)	(2630)
2	43900	(19500)	22902	12024	10873	(5897)	(2748)
3	43200	...	(23440)	...	(9820)	...	...
4	67266	...	...	...	...	...	...
Mean	48300	(19200)	21600	12644	9800	(5500)	(2700)

$FeSO_4$ M	0.146	0.169	0.169	0.169	0.161	0.176	0.146
H_2SO_4 M	.008	.23	.23	.23	.055	.012	.008
$CuSO_4$ M	.1	.05	.01	.001	.001	.001	.001
Expt.	$K_2 \times 10^5$						
1	2580	9109	(7134)	1960	2336	684	2860
2	2430	8213	6440	1701	(2175)	955	(2600)
3	...	...	...	...	(2360)	(1253)	...
Mean	2500	8700	6500	1830	2300	960	2730

The mean values in 0.23 *M* acid with varying concentrations of copper sulfate are plotted in Fig. 4; those obtained with 0.1 copper sulfate in varying concentrations of acid are plotted in Fig. 5.

These results show that copper sulfate has a pronounced effect on the oxidation of the ferrous salt solutions, and that, in sharp contrast with solutions containing no copper sulfate, the rate of oxidation increases rapidly with increasing acid concentration. It also appears that in 0.23 M sulfuric acid the accelerating effect of the copper sulfate increases markedly with its concentration, following quite accurately a logarithmic relationship. In lower concentrations of acid the increase with concentration is less marked, and at the lowest concentration there appears to be no well-defined change with the concentration.

Potassium Ferrocyanide Solutions.—It was of interest to measure the rate of oxidation of potassium ferrocyanide by gaseous oxygen be-

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[6] Chromic sulfate showed a slight depressing effect.

[7] Hess, Supplee and Bellis, *J. Biol. Chem.*, 57, *725* (1923); Quartaroli, *Gazz. chim. ital.*, 55, *252* (1925).

[8] Warynski, ***Ann. chim. anal.*, 14,** 45 (1909); Boselli, ***Compt. rend.*,** 152, 602 (1911); Meyerhof, "Chemical Dynamics of Life Phenomena," J. B. Lippincott Co., Philadelphia, 1924, p. 39; Reinders and Vles, ***Rec. trav. chim.*, 44,** 29 (1925).

cause, in contrast to the simple ferrous salts, it can be studied in neutral solution.

Potassium ferrocyanide can be titrated against permanganate in very dilute solution, when acidified, by the method of de Haën.[9] Solutions more concentrated than about 0.05 M, and especially solutions free from acid, deposit a precipitate of potassium manganese ferrocyanide.

We have, therefore, tried iodine for this titration. A 0.10013 M solution of freshly recrystallized and air-dried $K_4Fe(CN)_6{\cdot}3H_2O$ was prepared, and portions of it were shaken with an excess of a 0.0766 N solution of iodine under carbon dioxide. After fifteen minutes the excess iodine was titrated back with a 0.0985 N solution of thiosulfate. Two analyses of the stock solution by this method gave its normality as 0.09982 M and 0.10002 M, or on the average 0.09992, agreeing with the calculated value of 0.10013 to within two-tenths of one per cent.

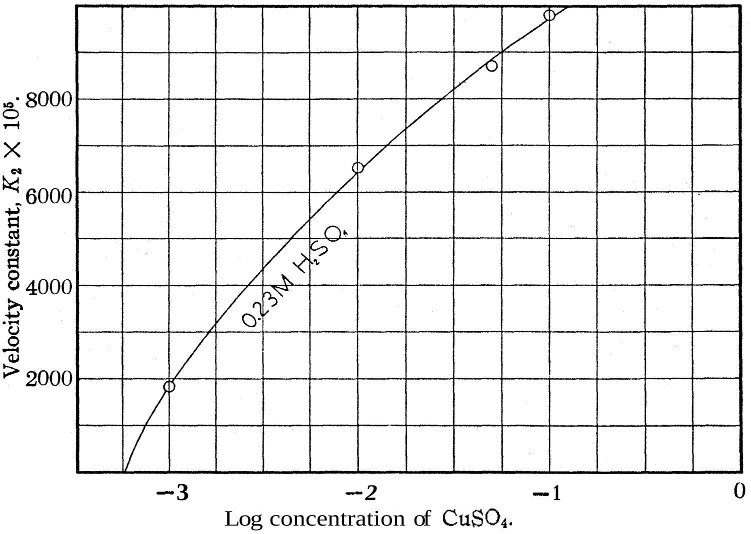

Fig. 4.—Variation of the velocity with the concentration of copper sulfate. $FeSO_4$, 0.15–0.18 M.

A calibration of the potential was carried out against known mixtures of ferro- and ferricyanide, using potassium iodide 0.5 M as a blank solution, by the method as outlined under the similar calibration of the ferrous–ferric potential. The results are given in Table XI.

Two oxygen absorption experiments were now run with a neutral solution of 0.150 *M* ferrocyanide, and identical values of $K_2 = 111 \times 10^{-5}$ were obtained. This shows that in neutral solution the ferrocyanide

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[9] De Haën, *Ann. Chem. Pharm.*, 90,160; also Treadwell–Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1919, Vol. II, 5th ed., p. 632.

TABLE XI

FERRO–FERRICYANIDE POTENTIAL IN $K_4Fe(CN)_6$ 0.150 *M*

AC as I_2	*AE* obs., mv.	Δ*E'* blank, mv.	*AE* corr.. mv.
0.00742	114.4	10.7	103.7
.01484	131.6	12.3	119.3
.02968	151.4	14.1	137.3
.03940	152.9	13.7	139.2

is oxidized about one-half as fast as is ferrous sulfate in solutions from 3 M to 0.01 *M* in sulfuric acid.

Two similar experiments were then made with portions of this same stock solution to which copper sulfate 0.001 M had been added. Values of $K_2 = 121$ and 151×10^{-5}, averaging 136×10^{-5} were obtained. It is evident that the copper sulfate produces no significant change in the velocity. This may be due to the fact that a precipitate of copper ferro- and ferricyanide is formed in the solution to which it is added, so that the copper ion may be present only in very minute amounts. It is of interest that the velocity of oxidation of the neutral ferrocyanide solution is substantially equal to that of the acid solutions of the ferrous sulfate. Either the ferrocyanide ion is directly oxidized by the gaseous oxygen, or the rapidity of oxidation of the ferrous ion in the neutral solution, in spite of its infinitesimal concentration, is tremendously greater than in the acid solution of the simple ferrous salts.

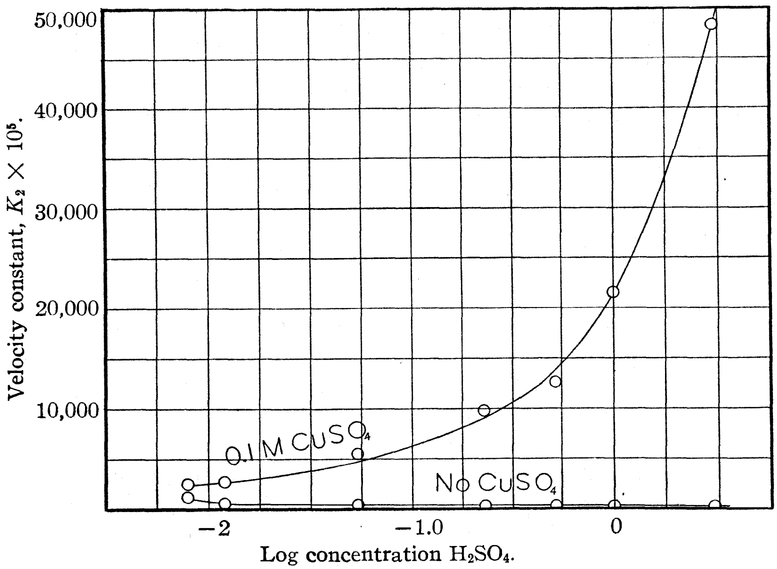

Fig. 5.—Effect of copper sulfate at various concentrations of sulfuric acid.

Solutions Containing Pyrophosphates.—Solutions of ferrous sulfate containing sodium pyrophosphate were found by Spoehr[10] to absorb oxygen rapidly, the originally green solution becoming deep red. Later Smith and Spoehr[11] measured the rate of the oxidation in order to ascertain the order of the reaction. These measurements were made by shaking 150 cc. of the solution with oxygen at constant pressure in a mechanically operated shaker making 120 strokes per minute. They found that the half-period of the reaction averaged about 57.5 seconds, irrespective of the concentration of the reactants. They concluded from this that the reaction was of the first order.

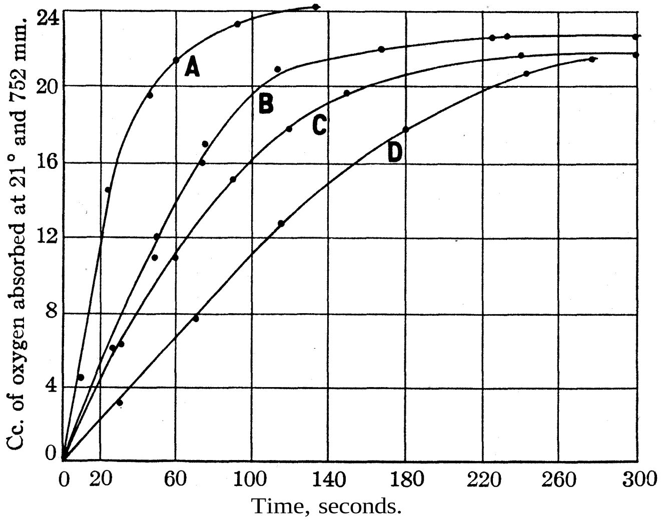

Fig. 6.—Velocity of oxidation of solutions containing pyrophosphate at different rates of stirring. A—170 r. p. m.; B—130 r. p. m.; C—120 r. p. m. (Smith and Spoehr); D—90 r. p. m.

We have repeated the measurements of Smith and Spoehr, adhering as closely as possible to the exact dimensions of their apparatus and to all the details of their procedure. With 150 cc. of a solution containing one gram of ferrous sulfate and 4.82 g. of sodium pyrophosphate, identical with that employed by them, and shaken at a rate of 130 strokes per minute, a half-period of about fifty seconds was obtained, confirming the numerical results of Smith and Spoehr as closely as could be expected.

However, we then repeated this experiment *at other rates of stirring. Our* results, together with the corresponding ones of Smith and Spoehr, are shown in Fig. 6.

It can be seen from these results that the velocity is largely a matter of the rate of stirring. Indeed, the half-period plotted against the rate of

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[10] Spoehr, THIS JOURNAL. 46, 1499 (1924).

[11] Smith and Spoehr, *ibid.*, 48, 107 (1926).

stirring gives a nearly linear curve. What is being measured is, therefore, not the rate of the chemical reaction itself, but a *rate of diffusion*. It is well known that this, in general, follows a logarithmic course and, therefore, simulates a first order reaction. The conclusion of Smith and Spoehr as to the order of the chemical reaction, based on these measurements, is, we believe, unwarranted.

In order to compare their results in ferro-pyrophosphate solution with our results in solutions of other iron salts, we have measured the rate of oxidation in this solution by our usual electrometric method. The potential change was calibrated in terms of oxygen by fitting to the apparatus of Smith and Spoehr an electrode, a salt bridge and a calomel electrode. The solutions were mixed under purified nitrogen, and the potentials observed before and after successive additions of pure oxygen, measured under known conditions of temperature and pressure in the calibrated buret included in the apparatus. A leveling bulb was attached to the buret for pumping and measuring the gas at atmospheric pressure. The oxygen introduced was not always completely absorbed, but the volume of gas absorbed was measured after ten minutes' shaking, after which no appreciable change in volume was observed. Under these conditions the potential measured before and after the volume measurement was the same to within ±0.2 millivolt. The results obtained, compared with those on a corresponding solution of ferrous sulfate and a similar solution of ferrous sulfate containing charcoal (to be described later), are shown in Table XII.

Table XII

Comparison of Results

	$FeSO_4$ 0.15 *M* $Na_2P_2O_7$ .023 *M*	$FeSO_4$ 0.15 *M* H_2SO_4 1.0 *M*	$FeSO_4$ 0.18 *M* H_2SO_4 1.0 *M* Charcoal 10 *g*.
E_C, v..........	−0.114	+0.361	+0.500
$K_2 \times 10^5$......	322000	279	318000
Eq. O_2/1 hr....	0.049	0.000053	0.038

It can be seen that the velocity of oxidation is indeed high, about 1000 times greater than in the ferrous sulfate solution. However, the potential is so very much lower that the solution is of little interest to us in the present investigation; indeed, it is scarcely more practical than such systems as the vanadous–vanadic, etc., previously referred to.

Heterogeneous Systems

The Effect of Coconut Charcoal.—A sample of granular, commercial, steam-activated coconut charcoal of the variety used in gas masks was ground in a mill and screened. Two lots were prepared, one of fineness between 60 and 100 mesh, and one finer than 100 mesh. Introduction of 1 g. of the 60–100 mesh material into 50 cc. of a 0.150 M $FeSO_4$–0.50 *M*

H_2SO_4 solution gave in duplicate experiments velocity constants (× 10^5) of 81,300 and 65,400, respectively. This is an increase of about 200 times, as compared with the velocity in the solution in the absence of the charcoal.

A series of experiments in duplicate was then made, using this same electrolyte, to find out the variation of the velocity with the amount of the charcoal. The average values of the velocity constant are given in Table XIII and are plotted in Fig. 7.

TABLE XIII

VARIATION OF THE VELOCITY WITH THE AMOUNT OF CHARCOAL

Solution: 0.150 M $FeSO_4$; 0.50 M H_2SO_4

Charcoal, g.	0.05	0.10	0.20	0.50	0.90	1.0	1.1	10.0
	K_2 × 10^5							
Expt. 1	(9380)	(18000)	26600	62400	79000	81300	88000	319000
Expt. 2	(5230)	(14600)	24500	50800	58600	65400	79400	173000
Mean	(7305)	(16300)	25500	56600	68800	71200[a]	83700	246000
Mean K_2 × 10^5/wt.	(146100)	(163000)	127500	113200	76444	73300	76100	246000

[a] Average of six experiments whose average deviation was ±6000.

These results show that the accelerating effect of the charcoal is approximately proportional to its amount. The slight decrease with amounts up to 1 g. and the considerable decrease with 10 g. may well be due to the less efficient stirring under these conditions.

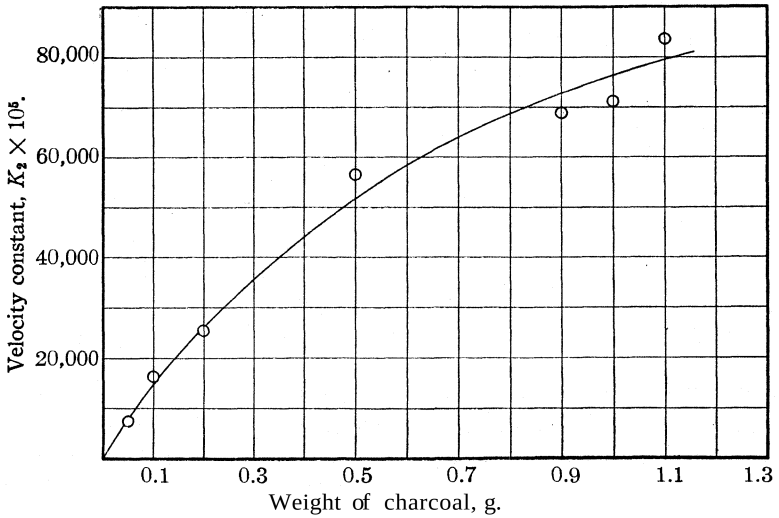

Fig. 7.—Variation of the velocity with the weight of the charcoal.

Two series of experiments were then made to find out the variation, if any, of this effect with the acidity of the ferrous sulfate solution. In one series 1 g. and in the other 10 g. of charcoal were used. The results are collected in Table XIV, and are plotted in Fig. 8.

Table XXV

Variation or the Effect of the Charcoal with the Acidity

Solution: 0.150 *M* $FeSO_4$

Charcoal	Concn. H_2SO_4	0.05	0.50	1.00	3.0
		$K_2 \times 10^5$			
	Series No. 1	(26600)	81300	....	45900
1 *g*. per 50 cc.	Series No. 2	(27800)	65400	....	37600
	Mean	(27200)	73300	....	41800
		$K_2 \times 10^5$			
	Series No. 3	21000	(319000)	305000	167000
10 *g*. per 50 cc.	Series No. 4	20900	(173000)	311000	149000
	Mean	20900	(246000)	308000	158000

It can be seen that with a constant amount of charcoal the velocity varies considerably with change in the concentration of the acid, a maximum velocity being reached in each case at 0.50 to 1.0 *M* acid.

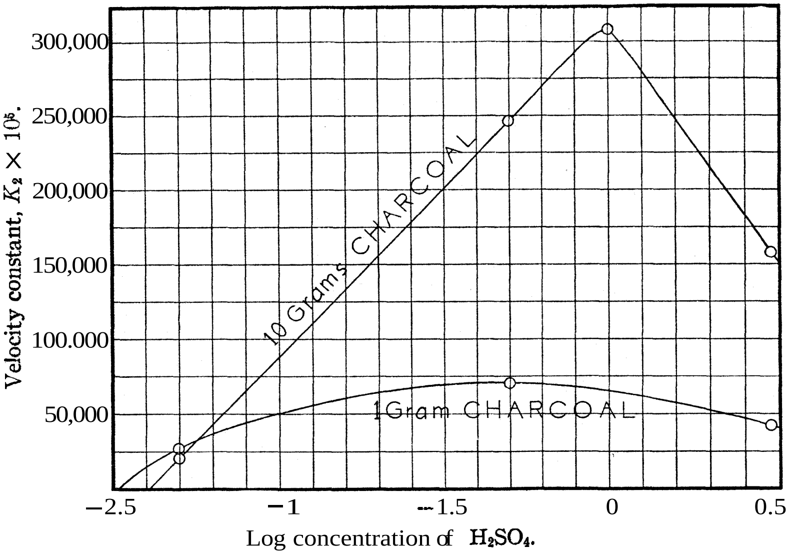

Fig. 8.—Variation of the velocity in the presence of charcoal with the concentration of the sulfuric acid. $FeSO_4$, 0.15 M.

Experiments were also made on the effect of charcoal on the rate of oxidation of solutions containing copper sulfate. The results of these experiments and of the corresponding blank experiments are collected in Table XV.

These results show that the velocities of oxidation with and without the copper sulfate are substantially the same, indicating that the action of the copper sulfate in the presence of the charcoal is either suppressed, or at most is only arithmetically additive.

To ascertain whether these data were significantly affected by the

TABLE XV

SIMULTANEOUS EFFECT OF CHARCOAL AND COPPER SULFATE

Solution: 0.150 *M* $FeSO_4$; 0.50 M H_2SO_4

Catalysts added	... ...	0.10 M $CuSO_4$ ...	.... 1 g. charcoal	0.10 M $CuSO_4$ I g. charcoal
$K_2 \times 10^5$	263 307	13300 12000	79500 67500	(77000) (66000)
$K_2 \times 10^5$ (Mean)	285	12600	73500	(72000)

alkaline ash of the charcoal (or by a possible preferential adsorption of sulfuric acid) 1-g. samples of charcoal of different degrees of fineness were each shaken with 50 cc. of 0.5 M sulfuric acid, filtered off by suction and the concentration of the filtrates determined by titration. It was found that the concentration had changed by about 2%, corresponding to a removal of about 0.0005 mole of sulfuric acid from the solutions by the charcoal. No significant variation of this percentage was observed with the different mesh sizes of the charcoal. This change in concentration is too small to have been of any significance in the above measurements.

Similar experiments were made with a solution 0.5 M in sulfuric acid and 0.01 M in copper sulfate. Here again about 2% of the acid was removed and about 1% of the copper sulfate. This latter result indicates that the apparent inactivity of the copper sulfate in the solution with charcoal could not have been due to its removal from solution by adsorption.

The Effect **of** Platinum Black.—Two grams of scrap platinum was converted into platinum black by the method of Willstatter and Jaquet[12] and this was dried overnight over sulfuric acid in a vacuum desiccator. Suspensions of 0.5 g. of this material in 50 cc. of a 0.15 *M* $FeSO_4$–0.5 M H_2SO_4 solution were subjected to oxidation with air, and velocity constants of (341,000) and (347,000), averaging (344,000) X 10^{-5} were obtained. Suspensions of only 0.25 g. of this material in the same volumes of the same solution gave a velocity constant of only 75,800 × 10^{-5}. This more than proportional decrease in the velocity with the smaller amount of catalyst suggested a possible progressive poisoning of the catalyst.

To test this, the platinum black catalysts were removed from the solution, thoroughly washed, then replaced in the cells with fresh 50-cc. portions of the original solution, and the velocity of oxidation of each suspension was again measured. The 0.5-g. sample gave a constant of (19,900); the 0.25-g. sample in two experiments gave constants of (17,400) and (17,600), averaging (17,500) × 10^{-5}. These low values show that the catalyst had indeed become much less active with use.

The Effect **of** Silica Gel.—A sample of a commercial silica gel was powdered to pass a 60-mesh (per inch) screen. A suspension of one gram of this material in 50 cc. of a 0.15 M $FeSO_4$–0.5 M H_2SO_4 solution gave an oxidation velocity constant of 865, corresponding to about a three-

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[12] Willstatter and Jaquet, Ber., 51, 767 (1918).

fold increase as compared with the velocity constant given by the same solution without the silica gel. This increase, while a decided one, is scarcely one one-hundredth of that produced by charcoal in this same solution, and is only one three-hundredth of that produced by half as much platinum black.

Discussion of the Kinetic Results

The unimolecular behavior of the gaseous oxygen in the oxidation of these solutions of ferrous salts agrees with the observations of McBain[13] made with solutions of ferrous sulfate and with those of Just[14] made in his study of the autoxidation of solutions of ferrous bicarbonate. Similarly, the bimolecular behavior of the ferrous sulfate agrees with the observations of McBain,[13] Ennos[15] and Boselli,[16] made with the same substance but not with those of Just made with ferrous bicarbonate. On the other hand, the relatively slight retarding effect of acid on the velocity of oxidation in the absence of catalysts (a decrease of only four times in passing from 0.008 to 0.23 M acid) is not compatible with McBain's hypothesis that the rate of oxidation of the solution is primarily determined by the rate of oxidation of the relatively minute hydrolyzed portion of the ferrous sulfate.[17] Even less compatible with this hypothesis are our measurements showing that in the presence of catalysts (copper sulfate or charcoal) the velocity of oxidation increases with increasing concentration of acid.

Our finding of the outstanding activity of copper sulfate in accelerating the oxidation of ferrous sulfate solutions by gaseous oxygen confirms the observations of Boselli[16] upon this substance, as contrasted with those of Banerjee,[18] and is in agreement with the work of Meyerhof,[19] Reinders and Vles[20] and others on the autoxidation of numerous other substances.

The outstanding fact established by our experiments is that the very substances, namely, charcoal, platinum and cupric salts, which hasten markedly the decomposition of hydrogen peroxide, particularly in the presence of ferrous salt solution,[21] also greatly accelerate the oxidation of ferrous salt solutions by gaseous oxygen. This parallelism at once suggests that the two phenomena may be intimately related.

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[13] McBain, *J. Phys. Chem.*, 5, 623 (1901).

[14] Just, *Z. physik. Chem.*, 63, 385 (1908); *Ber.*, 40, 3695 (1907).

[15] Ennos, *Proc. Cambridge Phil. Soc.*, 17, 182 (1913).

[16] Boselli, *Compt. rend.*, 152, 602 (1911).

[17] For the degree of hydrolysis of ferrous sulfate, see A. Krause, *Z. anorg. Chem.*, 174, 148 (1928).

[18] Banerjee, *ibid.*, 128, 343 (1923).

[19] Meyerhof, *Arch. ges. Physiol.* (*Pflügers*), 200, 1 (1923).

[20] Reinders and Vles, *Rec. trav. chim.*, 44, 1 (1925).

[21] See Lemoine, *Compt. rend.*, 162, 657, 702 and 725 (1916); Bohnson and Robertson, THIS JOURNAL, 45, 2493, 2512 (1923); Warburg, *Biochem. Z.*, 113, 257 (1921); 119, 134 (1921).

An alluring hypothesis to explain this parallelism would be as follows. Hydrogen peroxide might conceivably be formed slowly from oxygen and water. Once formed it would react relatively rapidly with the ferrous salt. The slowness of the oxidation of the ferrous salt solutions would then be due to the slow rate of formation of the hydrogen peroxide. Catalysts which accelerate the oxidation of the solutions would then do this by virtue of the acceleration of the formation of hydrogen peroxide. But, by the fundamental principles of catalysis, the very catalysts which hasten this formation of hydrogen peroxide from oxygen and water will correspondingly hasten the decomposition of hydrogen peroxide into these substances. On this hypothesis, then, the above-mentioned parallelism would be expected.

A difficulty with this attractive hypothesis is that from energetic considerations it appears that even the maximum possible partial pressure, that is, the equilibrium partial pressure, of hydrogen peroxide in a 1:1 gaseous mixture of oxygen and water vapor at room temperature is only of the order of 10^{-22} atmospheres.[22] The equilibrium concentration of hydrogen peroxide in a saturated aqueous solution of oxygen at room temperature would be correspondingly infinitesimal[23] and, therefore, apparently quite inadequate to bring about the relatively rapid oxidation of ferrous salt solutions by gaseous oxygen which does, indeed, take place when catalysts are present.

There are still other objections to this explanation. Goard and Rideal[24] found that copper salts do not catalyze the oxidation of ferrous salts by hydrogen peroxide in *acid* solutions. Again, while Bohnson and Robertson did find a marked accelerating effect of copper salts on the decomposition of hydrogen peroxide, a maximum effect was observed at very low concentrations of copper salt, while in our experiments the catalytic effect increased progressively with the concentration of the copper salt.

Another mechanism involving hydrogen peroxide which has been proposed recently by Jander[25] can be represented as follows

Slow, primary reaction	$2FeO + O_2 + H_2O = Fe_2O_3 + H_2O_2$
Rapid, following reaction	$2FeO + H_2O_2 = Fe_2O_3 + H_2O$

This mechanism obviates the thermodynamic difficulties of the former explanation. However, the activity of copper salts in catalyzing this reaction, in view of the above-mentioned observation of Goard and Rideal, would appear to exclude it.

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[22] Computed from the free energy data for this reaction given by Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, **1923,** p. 496. See also Lewis and Randall, THIS JOURNAL, 26, 1916 (1914).

[23] This same conclusion follows from computations by Baur based on data of Nernst, given in Abegg, "Handbuch," Leipzig, **1908,** Vol. II, 1, p. 99.

[24] Goard and Rideal, *Proc. Roy. Soc.* (London), **105A,** 163 (1924).

[25] Abegg's "Handbuch" Leipzig, **1930,** Vol. IV, **3d.** Section, 2d part, pp. B13–14.

It appears, therefore, to be unlikely that these explanations, in spite of their simplicity, can be correct. Apparently, hydrogen peroxide is not the effective actor in all of these oxidations. Instead, it is probable that specific intermediate compounds, presumably peroxides of the several catalysts themselves, are primarily formed, which either oxidize directly the ferrous salt more rapidly, or accomplish this same result by hastening the formation or decomposition of a peroxide of iron which many authors consider to be involved in the oxidation of ferrous salts.

Peroxide in the Charcoal.—In view of this likelihood that a specific peroxide is involved in the case of each catalyst, we tested for a peroxide in or on the charcoal. For this purpose we stirred a suspension of 2 g. of the previously mentioned 100 mesh charcoal in 100 cc. of distilled water for five minutes with a current of air. This charcoal was then filtered off and successive small portions were shaken with pure water, or with solutions of sulfuric acid of various concentrations. The charcoal was again filtered off and the filtrates added to separate portions of acidified starch–iodide solution. No color developed in the filtrates from the suspensions in water, but a deep and nearly constant color, indicating the presence of a peroxide, appeared in a few seconds with the filtrates from the suspensions in 0.5, 1.0 and 1.5 molar sulfuric acid. The color was considerably less intense with the filtrate from the suspensions in 2.0 M acid, so that there was an evident maximum of color development at about 1.0 *M* acid.

These observations indicate that a peroxide is present in this charcoal, which is either insoluble or inactive in pure water, and has its maximum solubility or activity in solutions of sulfuric acid at an acid concentration of about 1 M. The location of this maximum activity is in striking agreement with that of the maximum velocity of oxidation observed in our kinetic measurements, using this charcoal as a catalyst in solutions of sulfuric acid of various concentrations.

A rough titration indicated that 1 g. of the 100 mesh charcoal in 50 cc. of water produces in dilute sulfuric acid about 0.0001 equivalent of active oxygen.

Further tests using 0.1 M sulfuric acid showed (1) that a positive test for a peroxide is obtained when fresh, dry charcoal without any deliberate aeration is acidified under an atmosphere of carbon dioxide (in the absence of air); (2) that charcoal once extracted with acid gives no further test for peroxide when shaken with fresh acid in an atmosphere of carbon dioxide; **(3)** that the same sample of charcoal once extracted with acid can again be made to give an equally positive test for peroxide by shaking the residual charcoal with more water and air, and repeating the extraction with acid; (4) that this successive aeration and extraction by acid can be repeated at least twice, and usually several times, with the same sample of charcoal; *(5)* that no difference in behavior is observed if the suspension of charcoal is aerated first and then acidified immediately before filtration, or if it is first acidified and then aerated.

These observations indicate that this charcoal acquired a charge of the peroxide in the process of manufacture; that this can be removed by shaking with dilute sulfuric acid; that a fresh charge can be rapidly added by exposure to air; that this process can be repeated at least twice and that the re-oxidation will take place equally well in neutral or acid solutions.[26]

All of these conclusions and, in particular, the parallelism in acid solutions of various concentrations between the activity of the charcoal as a catalyst and its activity in liberating indirectly iodine from starch–iodide solutions harmonize with our above conclusions drawn from the kinetic measurements.

Narcotics.—To obtain further information as to the presence of a peroxide in the charcoal, we have made tests similar to those of Warburg[27] on the oxidation of cystine by charcoal and air. He found that minute amounts of certain substances markedly retarded on this oxidation. We have tested the effect of two of his substances, phenyl urea and amyl alcohol, and in addition acetanilide, on the oxidation of ferrous sulfate solutions by charcoal and air.

The phenyl urea was made from aniline hydrochloride and potassium cyanate;[28] the other two were commercial preparations and were used without further purification.

The kinetic results obtained, both in uncatalyzed and catalyzed systems, are shown in the following table (Table XVI).

It can be seen from these results that, while no effect is produced on the uncatalyzed reaction, a marked depression of the velocity results when even small amounts of these "narcotics" are added to the catalyzed reaction mixtures. A plausible explanation of these results is that the "narcotics" combine with or, in any case, render less active relatively minute active ingredients or products, presumably peroxides of the catalysts.

Direct Measurement of the Efficiency of **Depolarization.**—The above

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[26] De Saussure [Thomson's Ann. Phil., 6, 243 (1815)] and particularly Stenhouse [Pharmaceutical Journal, 13, 454–457 and 14, 328–330 (1854)] recognized the enhanced oxidizing power of oxygen adsorbed on charcoal. Calvert [J. *Chem. Soc.*, 20, 293 (1867)] showed that oxygen adsorbed on charcoal oxidizes ethyl alcohol to acetic acid, and ethylene to carbon dioxide and water. Degener and Lach [*Dinglers polytech.* J., 256, 519 (1885)] observed that freshly calcined animal charcoal, if thoroughly moistened and then exposed to the air and light, formed hydrogen peroxide and ozone. Hulett and Lowry [THIS JOURNAL, 42, 1408 (1920)] found that a slow reaction takes place at room temperature between coconut charcoal and oxygen, with the formation of a non-volatile oxide.

[27] Warburg, Biochem. Z., 113, 257 (1921); 119, 134 (1921); *Naturwissenschaften* 112, 862 (1923).

[28] Weith, Ber., 9, 820 (1876).

TABLE XVI

EFFECT OF NARCOTICS

$FeSO_4$ 0.150 *M*; H_2SO_4 0.5 *M*

	Uncatalyzed			Catalyzed					
	$K_2 \times 10^5$			$CuSO_4$ 0.1 M			1 g. Charcoal		
				$K_2 \times 10^5$			$K_2 \times 10^5$		
Narcotic	Blank	Narcotized	Relative narcosis	Blank	Narcotized	Relative narcosis	Blank	Narcotized	Relative narcosis
Phenyl urea satd. 0.02 *M*	287	...	..	12644	1857	0.147	71200	19900	0.280
Amyl alcohol 0.10 *M*	287	...	..	12644	2626	0.208	71200	16680	0.234
Acetanilide 0.04 *M*	287	303	1.05	12644	1426	0.113	71200	18825	0.268

kinetic measurements permit us, as we have seen, to evaluate the activity of the various catalysts studied in accelerating the oxidation of the ferrous sulfate solution. The greater the activity of the catalyst in this respect, the greater should be the activity of the system as a depolarizer. Wc have measured the efficiency of depolarization of certain of these systems directly by bubbling oxygen through them, surrounding an electrode through which a current was passed in such a direction as would tend to evolve hydrogen upon it. The single potential of this electrode when the oxygen is absorbed at a constant rate, that is, when a steady current is maintained, compared with the single potential of this electrode immersed in the same solution when no current is passing, is a measure of the efficiency of the particular system.

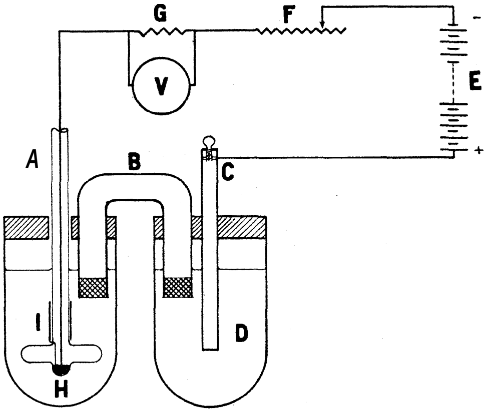

Fig. 9.—Apparatus for measuring the efficiency of depolarization.

The apparatus used for these measurements is shown diagrammatically in Fig. 9. A hollow stirrer from the previously described apparatus (Fig. 1) was provided with a sealed-in electrode (I) of polished platinum foil, connected by means of a mercury cup (H) at the bottom of the stirrer (A) with a copper wire leading through the hollow shaft of the stirrer to the battery (E). This arrangement provides a compact rotating air electrode on which concentration polarization is reduced to a minimum. The other pole, selected for its relatively slight tendency to polarize, consisted of a zinc bar (C) immersed in a saturated zinc sulfate solution (D) in a similar half-cell. The internal circuit between the two half-cells was completed by means of a saturated potassium chloride salt-bridge (B) in a pyrex glass tube of 8-mm. bore, plugged at each end with cotton wool. The external circuit, containing a 40-volt battery (E), a variable resistance (F) for current control and a milliammeter (G-V), is shown in the diagram. The external e. m. f. is imposed in such a way as to make the platinum electrode negative, *i.* e., to impress reducing conditions upon the air electrode. The relatively high potential of the battery was necessary to overcome particularly the resistance of the bridge. The milliammeter circuit contained a Weston millivoltmeter with a calibrated shunt resistance. The left-hand cell contained in addition a movable platinum electrode which could be immersed in the solution in order to determine its composition with respect to oxidizing and reducing ions. The single electrode potentials of this extra electrode and of the working (rotating) electrode were measured through a separate salt-bridge against the saturated calomel reference electrode in the usual way.

Our procedure was as follows. The solution of iron salt containing the catalyst was introduced into the left-hand cell and the air supply turned on. After a few preliminary readings on open circuit, the circuit was closed and the rheostat adjusted so that from 60 to 100 milliamperes flowed through the cell with the stirrer operating at 1250 r. p. m. Readings were then taken at intervals of the potential of the working electrode and that of the extra electrode. The difference between the two gives directly the polarization potential. Readings were continued until the potentials became constant or until it was evident that the potentials were not going to become constant.

Using this apparatus and procedure the efficiency of depolarization by gaseous oxygen was measured in the solution which had been found to exhibit the highest velocity of oxidation by gaseous oxygen. In making these measurements the circuit through the apparatus was closed at a predetermined instant and the current of air was then started. The observed values of the polarizing current and the potentials of the working and of the accessory electrodes are given in Table XVII.

It can be seen from these data that the initial closing of the circuit before the air supply and stirring had been started lowered considerably the potential of the working electrode. This potential rose slowly as the air supply was continued, reaching a nearly steady state at a potential of $E_h = +0.250 + 0.253 = 0.503$. When the current was now cut off and the air supply continued, the potential rose rapidly to that of the accessory electrode, $E_h = +0.410 + 0.253 = 0.663$. When the same current drain was again started after this preliminary aeration with no current flowing, the potential of the working electrode dropped only to $E_h = +0.353 + 0.253 = 0.606$ volt, indicating a polarization of only $+0.400 - 0.353 = 0.047$ volt. The measurements on the accessory electrode showed that no significant change occurred in the composition of the solution.

TABLE XVII

EFFICIENCY OF DEPOLARIZATION

50 cc. of solution: 1.1 M $FeSO_4$; 0.9 M H_2SO_4 + 10 g. of charcoal

Time, Hrs. min.	Current, m. a.	Potential Working electrode, $E_C = 0$, v.	Potential Accessory electrode, $E_C = 0$, v.
12:15	85.9	+0.199	.....
12:35	85.9	+ .213	
1:56	85.9	+ .241	
2:05	85.9	+ .247	.....
2:20	85.9	+ .247	.....
2:35	85.9	+ .250	
2:45	85.9	+ .250	.....
2:56	0.0	.....	+0.4060
3:00	.0	.....	+ .4059
3:08	.0	+ .4092	.....
3:11	.0	+ .4103	.....
3:15	85.9		+ .400
3:20	85.9	.....	+ .400
3:25	85.9	+ .352	.....
3:40	85.9	+ .354	.....
3:45	85.9	+ .352	
3:55	85.9	+ .353	

From these data the rate of oxygen absorption per liter of solution per hour can be calculated. It evidently equals (0.0859 X 3600 X 1000)/(96,500 X 50) = 0.0641 eq. of oxygen per liter per hour at an open circuit potential of +0.406 volt.

This rate of absorption can be compared with that found in the direct experiments on the velocity of oxidation. The data obtained in our experiments on solutions of this same composition at the same stirring rate of 1250 r. p. m. are collected in the following table.

TABLE XVIII

$FeSO_4$ 1.1 M; H_2SO_4 0.9 M; charcoal 10 g.

Expt.	Time, hrs.	ΔC, M	E_C, v.	Oxygen, eq./liter-hr.
1	1.88	0.118	+0.4147	0.0627
2	1.88	.102	+ .4104	.0543
3	3.80	.240	+ .4446	.0632
		Average	+ .423	.0601

It can be seen that the average rate of absorption of oxygen (0.0601) agrees closely with that found in the depolarization experiments (0.0641) being slightly less, as would be expected, at the somewhat higher potential (+0.423 as compared with 0.406). The agreement of these two results derived from such fundamentally different data affords very satisfactory evidence of their individual correctness.

In the following table the performance of one of these oxygen electrodes is compared with that of previous oxygen electrodes operating at room temperature, namely, the copper–cuprous oxide electrode of Hofmann[29] and the platinized carbon electrode of St. v. Náray-Szabó.[30]

TABLE XIX

EFFICIENCY OF SEVERAL OXYGEN ELECTRODES

Cell	Potential O_2 electrode, v.	Current, ma. Total	Current, ma. Density 100 cm.^{2}	Working potential O_2 elect., v.	Work, watts	Polarization, v.	Temp., °C.	
Air | Cu | CuO | 5% KOH | Cu | CO	0.92"	..	(80)[b]	0.2	0.016	0.72	20	Hofmann
O_2 | Plat.-Pt C | H_2SO_4 | $ZnSO_4$ H_2SO_4 | Zn	0.963	..	80	0.376	0.03	0.587	20	St. v. Náray-Szabó
Air | Pt | C $FeSO_4$ H_2SO_4 | H_2SO_4 | $ZnSO_4$ | Zn	0.659	86	2150	0.606	1.30	0.053	30	Lamb and Elder

[a] Potential of cell. [b] Estimated.

It can be seen that the present electrode, although it exhibits a lower open circuit potential, shows at a much higher current density a higher working potential, a much higher energy output and a much lower polarization. Indeed, it appears not to have been equaled in these respects except by the oxygen electrode of Baur operating at elevated temperature~. The relatively considerable activity of this electrode is to be ascribed not only to the intrinsic effectiveness of the catalyst, but also to the fact that it operates as a "bulk" as contrasted with a "surface" type of catalyst, as set forth in our introductory paragraphs.

These results were obtained with electrodes of 4 sq. cm. area immersed in 50 cc. of electrolyte. Assuming that a proportionate increase in these dimensions would be without effect on the efficiency of this electrode and that the normal hydrogen electrode with which it is in series is unpolarized and of negligible internal resistance, the cell would have an energy output of 0.94 watt per liter, or 0.94 kilowatt per cubic meter of electrolyte. These assumptions as to the hydrogen electrode are obviously ideal; but it does not appear improbable that a much more favorable ratio between the area of the electrode and the volume of the electrolyte than that used in our experiments might be secured, so that an even higher energy output per unit of volume might well be realized. **A** discussion of these matters, however, lies outside the scope of this article.

Summary

1. In an attempt to overcome by means of catalysts the well-known sluggishness of the oxygen electrode, the kinetics of the reaction between solutions of ferrous sulfate and gaseous oxygen has been re-investigated, particularly with reference to the accelerating effect of various secondary

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[29] Hofmann, Ber., 51, 1531 (1918).

[30] St. V. Náray-Szabó, Z. *Elektrochem.*, 33, 18 *(1927)*.

[31] Baur, *Helv. Chim. Acta*, 4,325 (1921).

or accessory catalysts. For this purpose an electrometric method was perfected for ascertaining the progress of the oxidation, which is independent of the, at present, unknown activity coefficients of the ferrous and ferric ions in these solutions.

It has been found from the measurements thus made (a) that the reaction is unimolecular with respect to the oxygen, and bimolecular with respect to the ferrous sulfate; (b) that the velocity of the reaction is independent of the concentration of the sulfuric acid at concentrations of 0.1 molar and higher, but increases progressively at lower acidities; (c) that a large number of metallic ions are without noticeable effect but copper ions have a pronounced accelerating effect; (d) that coconut charcoal and platinum black have pronounced accelerating effects, while silica gel is inactive; (e) that the accelerating effect of the charcoal reaches a maximum in 1 molar acid.

The conclusion is drawn that specific peroxides are presumably responsible for the accelerating action. Confirming this, a peroxide-like substance has been extracted in minute amounts from the aerated coconut charcoal, while several so-called narcotics have been found to have a pronounced depressing effect on the velocity of the reaction when catalyzed either by charcoal or by copper salts.

2. Neutral solutions of potassium ferrocyanide have been found by similar measurements to oxidize about half as rapidly as do corresponding solutions of ferrous sulfate in 0.01 to 3.0 molar sulfuric acid. Copper salts are here without significant effect.

3. Solutions of ferrous sulfate containing sodium pyrophosphates have been found to oxidize about 1000 times faster than ferrous sulfate in 0.1 to 3.0 molar sulfuric acid. Their oxidizing potential is, however, nearly half a volt lower. The conclusion previously reached by others that this is a reaction of the first order with respect to the ferrous salt has been shown to be based on an error of interpretation.

4. Direct measurements of the depolarizing activity of ferrous sulfate solutions containing certain of these accessory catalysts have been made. Electrodes utilizing these solutions exhibit, as compared with previously studied oxygen electrodes at room temperature, at a higher current density, a higher working potential, a higher energy output and a much lower polarization.

5. The rates of absorption of the oxygen in these direct measurements of depolarization have been found to check closely the rates of absorption determined in a very different way in the kinetic measurements.

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NOTES

A Note on the Preparation of Iodine Trichloride.—The authors were confronted recently with the problem of preparing two kilograms of iodine trichloride, sealed in glass ampoules in 50-g. quantities. Trial of the most promising methods suggested in the literature showed them to be unsuited for the preparation of a definite quantity of this relatively unstable material in place in glass tubes. The following very satisfactory method was worked out, and is described here because of the great economy of time and material which it effected.

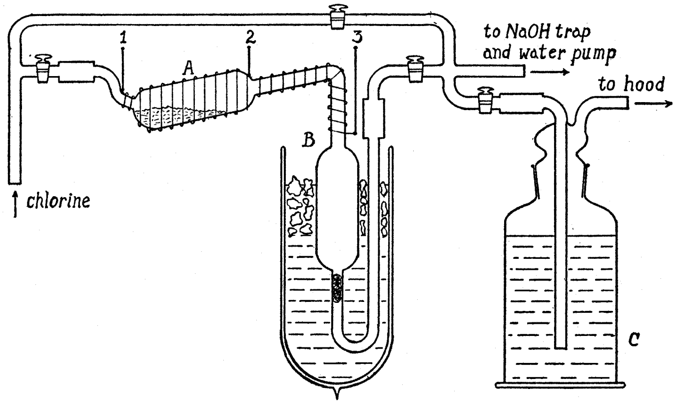

Fig. 1.—Apparatus for making iodine trichloride.

A slight excess of iodine was placed as shown in tube A, Fig. 1, before A and B were sealed together. The tubes were then placed in the system and B was immersed in ice water to a point 2 cm. from the bottom. The connecting tube between points 2 and 3 was heated electrically to about 100° to prevent deposition of the trichloride. Chlorine was then allowed to flow through the system at the rate of 80–90 cc. per minute until the iodine appeared to be completely,liquefied owing to the formation of the monochloride. Some trichloride was also formed and was deposited mainly in the lower end of B on the loose plug of glass wool, thus helping to prevent the loss of the larger quantity of trichloride which came over later. The electrical heating was then extended to include A and was adjusted so as to keep the liquid monochloride just below its boiling point (100°). The ice water-bath around B was raised to a point I cm. from the top of this tube for the remainder of the run. The rate of flow of chlorine was increased to about 170 cc. per minute. At the conclusion of a run the system was partially evacuated, the tubes were disconnected at the rubber joints, which were closed with screw clamps, and B was carefully sealed off at a convenient place at each end.

It was found that a rate of flow of chlorine faster than that stipulated or especially a temperature high enough to boil the liquid in A resulted in a too rapid deposition of the trichloride in B, with consequent plugging of this tube. The size of the tubing employed in construction of the apparatus was also found to be important. If B was less than 3 cm. in diameter or less than 9 cm. long, the deposit of trichloride invariably plugged up the tube so as to stop the flow of chlorine, thus forcing the system apart at one of the rubber connections, or at best nearly doubling the time required for a run owing to the decreased rate of sublimation of the trichloride. The tubing connecting A and B was 1 cm. in diameter, and the rest of the system was constructed of 8-mm. tubing, pyrex glass being used throughout. It was also found that if the final position of the cooling bath around B was higher than that indicated, plugging of the trichloride was likely to result.

Under the above conditions a dense core of iodine trichloride, light orange in color and containing only traces of monochloride, was formed in B, leaving no residue in A and resulting in only a slight loss of product beyond the glass wool in B. Small amounts of the trichloride were decomposed to the monochloride in the final sealing-off process. To produce 50 g. of product, 27.2 g. of iodine is required; 30-g. samples of iodine were used, yielding slightly more than 52 g. of product. The time required was slightly more than two hours per sample, including the necessary glassblowing.

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RECEIVED OCTOBER 21, 1930
PUBLISHED JANUARY 12, 1931

The Analysis of Dilute Iodine Solutions.—The investigation of a reaction system comprising iodine, iodate ion and hydrogen peroxide required the accurate determination of the rate of disappearance of iodine when the amount initially present in a sample was less than 3 mg. From time to time the iodine was extracted with about 25 cc. of carbon tetrachloride, enough of the aqueous solution being taken to supply iodine equivalent to 1 to 5 cc. of 0.004 N sodium thiosulfate. The details of the method which enabled satisfactory determination of iodine even at concentrations below 10^{-5} M in the aqueous solution are as follows.

The carbon tetrachloride containing the iodine is transferred to a 500-cc. glass-stoppered flask containing approximately 50 cc. of a 1% potassium iodide solution, made sufficiently acid (about 0.001 N) to neutralize any basic substance added as preservative to the sodium thiosulfate solution. Freshly prepared 0.004 N thiosulfate is then run in until the carbon tetrachloride layer is practically colorless after shaking; 5 cc. of starch solution is then added, and the end-point taken as the mid-point of the drop which causes the last trace of bluish color to disappear from the carbon tetrachloride layer.

On moderate shaking after the addition of the starch, the carbon tetrachloride layer remains in small bubbles of which the surface is blue even when the aqueous layer has been rendered entirely colorless in the approach to the end-point. Since the starch tends to remain in the water layer while the iodine tends to become concentrated in the carbon tetrachloride, conditions in the interface between the two layers are particularly favorable for the formation of the blue starch–iodine compound. With practice, the drop of thiosulfate which causes the removal of the last trace of this color can be easily observed—the more so since the carbon tetrachloride layer on shaking often assumes a slight yellow tinge when all of the iodine has gone. This combination of the starch and carbon tetrachloride end-points is advantageous since it permits concentration of the iodine, which the starch end-point does not, and since, in the presence of the I^- essential to satisfactory titration of iodine with sodium thiosulfate, it is more sensitive than is the carbon tetrachloride end-point alone.

Under the most favorable conditions $4(10^{-5})$ g. of iodine in 40 cc. of aqueous solution, corresponding to a concentration of 4×10^{-6} *M*, could be detected by the above method; the starch solution when used alone permitted the detection of iodine in a 2×10^{-6} M solution, a value for the sensitiveness which agrees with earlier results obtained by Dr. H. E. Miller of this Laboratory. The starch solution was prepared by a method similar to that of Mutnianski,[1] recently described by Kolthoff,[2] except that potato instead of "soluble" starch was used. When potato starch is used, the solution must be boiled for a short time after the starch is added. Decantation after allowing suspended matter to settle insures a clear solution.

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RECEIVED NOVEMBER 1, 1930
PUBLISHED JANUARY 12, 1931

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[1] Mutnianski, *Z. anal. Chem.*, 36, 220 (1897).

[2] Kolthoff, "Volumetric Analysis," Vol. II (1929), pp. 349 et *seq.* The sensitiveness for "soluble" starch under the best conditions is given on p. 350 as 1 to 2×10^{-5} N, *i. e.*, 5 to 10×10^{-6} *M* I_2.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

X-RAY INVESTIGATIONS OF OPTICALLY ACTIVE COMPOUNDS. II. DIPHENYL AND SOME OF ITS ACTIVE AND INACTIVE DERIVATIVES[1,2]

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RECEIVED JUNE 23, 1930 PUBLISHED JANUARY 12, 1931

The problem to which this x-ray diffraction analysis is being applied as a mode of attack is that of the stereoisomerism of derivatives of diphenyl. It is known that the substitution of certain groups in the 2,2′,6,6′-positions of diphenyl gives compounds which may be resolved into stereoisomers. Many of these compounds have been prepared by Dr. Roger Adams[3] and his students for the purpose of determining which groups give rise to this effect. It is thought that the presence of sufficiently large groups prevents a free rotation of the two rings and hence two active forms of such a compound exist The crystallographic examination was undertaken in order to find, in the crystal at least, the positions, symmetry, and approximate shape of the molecules of the derivatives of diphenyl, and to see whether there is any differentiation apparent in the crystalline structure between those compounds which resolve into active isomers and those which do not.

Experimental

1. General Methods Employed

(a) Preparation of Sample.—Well-formed crystals of the substance under investigation were prepared by the slow evaporation of a barely saturated solution protected from dust. A single crystal, preferably one millimeter in its longest dimension, was selected for mounting. This was examined under the microscope for vibration axes and mounted either by eye or under the microscope on a glass fiber which was then attached to a goniometer head.

(b) A Rotation Photograph.—Rotation and oscillation photographs were used in the greater part of this work. The single crystal, mounted so that an important crystallographic direction was parallel to the axis of rotation, was rotated in a pin-hole defined beam of copper radiation from a Siegbahn–Hadding or Shearer gas-type tube. Inasmuch as the general radiation is inappreciable in intensity and the Kα can easily be distinguished from the Kβ, unfiltered radiation was employed in practically all of the work. A circular camera of 5-cm. radius surrounded the crystal as a center. Exposures varied from two to eight hours depending on the focus of the beam and the size and absorption of the crystal.

When the crystal was lined up with the crystallographic axis coinciding with the

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[1] For the first paper in this series see Clark and Yohe, THIS JOURNAL, 51, 2791 (1929).

[2] Part of a thesis submitted by Lucy W. Pickett to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy

[3] Hyde and Adams, THIS JOURNAL, 50, 2499 (1928); Moyer and Adams, *ibid.*, 51,630 (1929); Stanley and Adams, *Rec. trav. chim.*, [4] 48,1035 (1929); THIS JOURNAL, 52, 1200 (1930).

axis of rotation, the photograph consisted of spots arranged in straight rows. If the two axes made an angle with each other, this was evidenced by the fact that the central line of spots was split into two lines crossing each other at an angle which is twice the angle between the axis of the crystal and the axis of rotation. Thus a correction could be made in the goniometer setting and the correct lining up of the axis obtained by somewhat of a trial and error process. The rows of spots in the photograph are termed layer lines, the one containing the undeviated beam being the 0 line and the others numbering 1, 2, 3, etc., from that line.

The unit length along the axis of rotation may be calculated directly from the photograph through the use of the relation $I \sin \Phi = n \lambda$ where λ is the wave length of the radiation used (1.54 for Cu-Kα), n is the number of the layer line, I is the desired unit, and Φ may be measured as the angle whose tangent is the distance from the 0 layer line to layer line n, divided by the distance from crystal to film.

Rotation pictures can then be taken about the other two axes, and their position measured from the settings on the goniometer head From measurements of the layer lines of each of these, the dimensions of the unit cell are directly obtained.

The number of molecules in the unit cell may be calculated from these data together with the experimentally measured density of the crystal by means of the following formula

$$a \times b \times c \times \sin \beta = \frac{\text{mol. wt. X n}}{\text{Avogadro's number}} \times d$$

a, b and c are lengths of the unit cell expressed in cm., d is density and n is number of molecules in the unit cell.

The assignment of indices to the spots on the films is the next step and is attended with somewhat more difficulty. In a rotation photograph about the c axis, for instance, reflections from all the planes with index $hk0$ are present in the zero layer line, while planes of the hkl series reflect in the first layer line, $hk2$ planes in the second layer line, etc. The spacings corresponding to the spots on the zero line can be calculated by means of the usual Bragg formula $n\lambda = 2d \sin \Theta$. Furthermore, spots with the same h and k indices lie on lines which are curved but nearly vertical in general. The exact position of these lines has been worked out. In spite of these very helpful principles, the complexity of the photographs makes a certain identification of the spots difficult and two devices were employed in this work to make the identification less arduous.

One was the construction of a table which gave for each distance on the film under the conditions used the corresponding interplanar spacing. Thus, once the table was constructed, a large number of individual calculations was avoided.

The second was the use of oscillation photographs to analyze and simplify the diagram. Instead of rotating the crystal through 360°, it was oscillated 15° at a time, and a series of overlapping oscillation pictures were taken. As there were fewer spots on each of these, each spot could be identified with more certainty, especially as one could calculate from the position of the crystal whether the plane which was suspected could have been in position within that 15° oscillation to give a reflection.

(c) A Laue Photograph.—To aid in determining the symmetry in certain cases Laue photographs were taken. Unfiltered molybdenum radiation was employed for this purpose, and the crystal was mounted in a pin-hole beam so that the beam was parallel to a crystallographic axis. If the alignment was perfect, a symmetrical design of spots was obtained, to which indices could be ascribed after a gnomonic projection.

(d) Assignment of Space Group.—Astbury and Yardley[4] have compiled tables in which the missing reflections characteristic of each of the **230** space groups are listed. After the spots have been identified by the method described in the previous section, the classes which are consistently absent are noted and the space group found from reference to the tables. Often several space groups have the same missing reflections, in which case the number of molecules in the unit cell, the external symmetry, and other information about the crystal may help to clear the ambiguity. Further information must be obtained by individual methods varying with the substance used.

2. Data for Crystals

(a) **Diphenyl.**—The commercial product was purified by recrystallization four times from 95% alcohol followed by a slow recrystallization from absolute alcohol. Diphenyl crystallizes in thin flat plates with the 001 planes as the extended face and shows preferred cleavage along the a and b axes. The crystal unit was found to be monoclinic with the dimensions $a = 8.11$, $b = 5.67$, $c = 9.57$, $\beta = 94.5°$. After this work was completed. an analysis by Hengstenberg and Mark[5] was found in which the following dimensions were obtained: $a = 8.22$, $b = 5.69$, $c = 9.50$, $\beta = 94.8°$. The two sets of data show very fair agreement. An analysis of the spacings showed that the reflections from all of the planes $h0l$, where h is odd, were absent as well as those from the $0k0$ planes where k is odd. This indicates that the structure is of monoclinic prismatic type and belongs to the space group C_{2h}^5, which is based on the simple monoclinic lattice. From the fact that the density of diphenyl is 1.165, the number of molecules in the unit cell must be 2. The space group C_{2h}^5 requires 4 asymmetric molecules in the unit cell or two molecules each of which contains a center of symmetry and therefore diphenyl in the crystalline state must possess centro-symmetry.

There are four possible equivalent positions for two molecules which may be expressed analytically as follows

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[4] Astbury and Yardley, *Phil. Trans.* Roy. *Soc* (London), **A224,** 221 (1926).

[5] Hengstenberg and Mark, *Z. Krist.*, **70,** 285 (1929).

(a) $^1/_4\,^1/_4\,0;\ ^3/_4\,^3/_4\,0$

(b) $^1/_4\,^1/_4\,^1/_2;\ ^3/_4\,^3/_4\,^1/_2$

(c) $^1/_4\,^3/_4\,0;\ ^3/_4\,^1/_4\,0$

(d) $^1/_4\,^3/_4\,^1/_2;\ ^3/_4\,^1/_4\,^1/_2$

(b) **Dimesityl.**—Dimesityl crystallizes from an alcohol–water mixture in colorless rectangular plates or in needles. The product used was obtained prepared in this Laboratory from Dr. Stanley. Its density, determined by immersing a crystal in an aqueous salt solution of the same density, is 1.020.

Rotation and oscillation pictures indicated the following dimensions: $a = 8.21$, $b = 8.58$, $c = 22.25$, $\beta = 96.30°$. There are, therefore, four molecules in the unit cell.

A table showing the relative intensities of the reflections noted is found in Table I. A scrutiny of this table reveals the fact that the planes $h0l$ where 1 is odd as well as the plane 010, show no reflection. The only space group that fits these facts is C_{2h}^5 based on the simple monoclinic lattice Γ_m. Either two molecules with a center of symmetry or four asymmetric molecules may be placed in one unit cell in this space group. Hence the dimesityl molecule must be asymmetric.

The equivalent positions in this space group may be expressed by the coordinates $xyz;\ x, y + {}^1/_2, \bar{z};\ x + {}^1/_2, \bar{y}, z;\ {}^1/_2 - x, {}^1/_2 - y, \bar{z}$.

(c) **3,3′-Diaminodimesityl.**—This compound has been resolved into two active forms by Adams and Moyer. Samples of each of these were loaned for crystal analysis. The compound formed fine crystals and proved very difficult to obtain in crystals large enough to work with. After repeated trials lasting over several months, one crystal of the 1-form was obtained, and soon after a very tiny crystal of the d-form. The crystals formed in six-sided, colorless, slightly yellow plates from an alcohol–water mixture containing about 80% alcohol.

A very complete series of oscillation photographs of the former was taken. Powder photographs of the d- and I-forms showed the same spacings, and the few oscillation photographs of the d-form which were taken were exactly like those of the 1-form in a similar position. Thus it was concluded that the d- and I-forms were identical as regards x-ray reflection, a fact which has been noted before where stereoisomers were concerned.

The dimensions of the unit cell were calculated as a = 8.26, b = 8.58, c = 22.62. The three axes were obtained at right angles to each other on the goniometer. The number of molecules in the unit cell is four.

The photographs obtained were so nearly similar to those of dimesityl that they might easily have been mistaken for each other. A detailed comparison of the intensity of the individual spots is presented in Table I. It may be seen from the table that those reflections are missing for the planes $h0l$ where I is odd, while 010 is either missing or extremely weak. Although the angle β cannot be distinguished with absolute certainty from 90°, the similarity to dimesityl indicates that the space groups are probably the same, C_{2h}^5, and that β is within 30' of 90°.

TABLE I

COMPARISON OF INTENSITIES OR REFLECTIONS FROM DIMESITYL AND *l*-3,3'-DIAMINO-DIMESITYL

Planes	Dimesityl	Diamino-dimesityl	Planes	Dimesityl	Diamino-dimesityl
001	0	0	101	0	0
002	7	5	102	5	6
003	0	0	103	0	0
004	7	7	104	4	7
005	0	0	105	0	0
006	6	7	106	4	6
007	0	0	107	0	0
008	5	5	201	0	0
010	0	1	202	4	5
020	5	6	203	0	0
011	1	1	110	1	2
012	6	7	210	5	6
013	5	5	220	7	6
014	4	4	310	0	1
015	4	2	410	0	0
016	5	5	211	4	5
017	4	4	212	5	6
021	0	1	213	4	5
022	4	4	214	2	1
023	4	1	215	2	4
100	7	7	311	2	4
200	6	5	312	2	4
300	1	1	313	2	3

0 absent; 1 very weak; 2 weak; 3 medium weak; 4 medium; 5 medium strong; 6 strong; 7 very strong.

(d) **Hexachlorodiphenyl.**—The photographing of hexachlorodiphenyl involved a difficulty not encountered in any of the foregoing work in that the compound because of its many chlorine atoms is highly absorptive to the copper radiation. On this account very small crystals were used and longer exposures were necessary.

Hexachlorodiphenyl was prepared by Mr. Julius White in this Laboratory. It crystallizes from alcohol in colorless six-sided tablets. Optical measurement disclosed a monoclinic habit of the crystal with $\beta = 88°$. Three photographs at right angles showing clearly defined layer lines were obtained and the dimensions of the unit cell calculated as follows: a = 15.80, b = 8.54, c = 10.74. A closer examination of the diagrams about the c axis showed that very faint lines of spots lay between those taken as the layer lines and hence that the above c dimension should be doubled. Thus the true dimensions of the unit cell are a = 15.80, b = 8.54, c = 21.48.

The following spots were identified as present: 002, 004, 022, 024, 026, 020, 013, 015, 200, 400, 210, 310, 410, 320, 420, 520, 202, 204, 120, 210, 310, 110, 220, 330, 111, 112, 113, etc., while 001, 003, 010, 012, 014, 100, 300, 102, 103, 104, 105 were absent. This may be summarized by stating that interferences for those planes are absent which have indices Okl where $k + l$ is odd, and $h0l$ if h is odd.

The density as measured by the flotation method in a sulfuric acid and water mixture was 1.655. The number of molecules in a unit cell calculated from this figure is 7.98 or 8.

The only space groups in the orthorhombic or monoclinic systems which have the above mentioned spacings absent are C_{2v}^{9} and Q_h^{16} (also written V_h^{16}). The first allows for only four asymmetric molecules in the unit cell and hence would necessitate the assumption of polymerization. The second allows eight asymmetric molecules and hence is the more probable.

The space group Q_h^{16} has eight equivalent positions as follows: xyz; $x + {}^1/_2, {}^1/_2 - y, \bar{z}$; $\bar{x}, y + {}^1/_2, {}^1/_2 - z$; ${}^1/_2 - x, \bar{y}, z + {}^1/_2$; ${}^1/_2 - x, {}^1/_2 - y, \bar{z}$; $\bar{x}yz$; $x + {}^1/_2, \bar{y}, z + {}^1/_2$; $x, y + {}^1/_2, {}^1/_2 - z$.

After an optical examination indicated a monoclinic form while the x-ray data very clearly indicated an orthorhombic space group, all of the diffraction films were carefully reexamined. It is absolutely impossible to fit these data to any monoclinic space group, so the conclusion is that the crystal was not sufficiently perfect to enable unambiguous microscopic examination or else that the crystal actually has an outer pseudo-monoclinic form. There can be absolutely no question concerning the clear-cut x-ray data.

(e) Diphenic Acid.—Diphenic acid crystallizes readily from an acetic acid and water mixture in colorless six-sided tablets. Its density as determined by flotation in a sulfuric acid and water mixture is 1.40 It exhibits parallel extinction between two crossed nicol prisms.

An optical examination by Dr. E. T. Wherry of the U. S. Department of Agriculture of diphenic acid crystals disclosed the following facts. Making the shortest dimension axis a and the longest axis c and then making the prism (120) and the side-dome (011) gives

Axis c = **tan** ρ of (011); p *observed* 49°; $c/b = 1\ 15$
Axis a = **cot** ϕ of (120); ϕ *observed* 59°; $a/b = 1.20$

Rotation photographs of three axes at right angles to each other were taken in the usual manner. The dimensions of the unit cell were calculated as a = 13.80, b = 11.90, c = 14.12 with eight as the number of molecules in the unit cell with b = 1, $c/b = 1.15$ and $a/b = 1.19$, in excellent agreement with optical data. A series of oscillation pictures indicated that the following planes gave reflections: 002, 003, 004, 006, 106, 107, 108, 109, 116, 117, 118, 126, 127, 012, 014, 021, 022, 023, 024, 200, 110, 310, 211, 221, 020, 012, 032, 022. Inspection shows that the following set of planes are definitely present; hkl where $h + k + l$ is odd, Okl where $k + 1$ is odd, $h0l$ where $h + l$ is odd, $hk0$ where h or k is odd, $0kl$ where k or l is odd, $h0l$ where h or l is odd. None of the planes $hk0$ for which $h + k$ is odd are present. The following planes are definitely absent: 310, 410, 010, 030, 100,300,011, 013, 031, 033. The first six of these are characterized by the classification, $hk0$ where h + k is odd. The last four are probably missing for some other reason than that of space groups, Only those planes have been listed which could be identified without ambiguity, though further inspection strengthened the conclusion that only those planes were consistently absent which had the indices $hk0$ where h + k is odd.

The only space group which necessitates this particular spacing is the orthorhombic group Q_h^{13} (V_h^{13}) based on the simple orthorhombic lattice. This group contains eight unsymmetric molecules in the unit cell. Hence the diphenic acid molecule possesses no symmetry in the crystalline state, a result to be anticipated from the formula. The eight equivalent positions in this space group may be expressed analytically: X, y, z; $X + {}^1/_2, {}^1/_2 - y, \bar{z}$; ${}^1/_2 - x, y + {}^1/_2, \bar{z}$; $\bar{x}, \bar{y}, z$; ${}^1/_2 - x, {}^1/_2 - y, \bar{z}$; $\bar{x}, Y, z$; $x, \bar{y}, z$; $x + {}^1/_2, y + {}^1/_2, \bar{z}$.

(f) *o*-Tolidine.—The tolidine used was prepared in this Laboratory as the crude product and purified in the following manner: 10 g. was suspended in hot water and hydrochloric acid added to form the soluble hydrochloride. This was boiled with norite for twenty minutes, filtered hot, allowed to cool somewhat and neutralized with sodium hydroxide. The product was recrystallized from 80% alcohol. It crystallized nicely in rectangular tablets slightly brown in color.

An examination under the polarizing microscope showed that the crystals exhibit parallel extinction. An optical examination by Dr. Wherry proved the crystals to be orthorhombic. According to the classification of Wherry and Adams,[6] the material is endo-rhombic, but often ecto-monoclinic. With the longest dimension of the crystal oriented as axis a, and the shortest dimension c, the front-dome (101) and the side-dome (102), the measurements gave

Axis $c = {}^1/_2 \tan \rho$ of (012); p observed 57° 30'; $c/b = 3\ 14$
Axis $a = c/\tan \rho$ of (101); ρ observed 75°; $a/b = 0.84$

Examinations by Laue, rotation and oscillating crystal methods revealed the unit cell as orthorhombic with the dimensions $a = 6.50$, $b = 7.48$, $c = 23.62$ Å.; with $b = 1$, $c/b = 3.15$ and $a/b = 0.86$, in excellent agreement with the optical data. The density was determined as 1.215 and from this the number of molecules in the unit cell was found to be four.

The 001 planes where 1 is odd, and the $h00$ planes where h is odd are definitely absent, while the $0k0$ planes where k is odd are either absent or extremely weak. No other class of reflections is absent. Hence the space group is either the orthorhombic group Q^3 or Q^4 (V^3 or V^4). There is the possibility that the crystal might be monoclinic with an angle of 90 ± 0.5°

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[6] Wherry and Adams, *J. Washington Acad. Sci.*, 9, 153 (1919).

and hence belong to the space group C_{2h}^2. In any case the molecule is asymmetric since there are four molecules in the unit cell.

The following table summarizes the results obtained for the crystal structures of the compounds.

		Unit cell dimensions						
	System	a	b	c		n	Space group	Symmetry of molecule
Diphenyl	Mono.	8.11	5.67	9.57	94°30′	2	C_{2h}^5	Center of symmetry
Dimesityl	Mono.	8 21	8 58	22 25	96°30′	4	C_{2h}^5	None
3,3′-Diaminodimesityl	Mono.	8 26	8 58	22 62	90° ± 30′	4	C_{2h}^5	None
Hexachlorodiphenyl	Orth.	15 80	8 54	21 48	90°	8	Q_h^{16}	None
o-Tolidine	Orth.	6 50	7.48	23 62		4	Q^4	None
Diphenic acid	Orth.	13 80	11 90	14 12		8	Q_h^{13}	None

Discussion of Results

The table just preceding summarizes the information which may be deduced directly from the x-ray data. Without accurate measurements of intensities and interpretations based thereon, statements concerning the disposition or size of molecules within the crystal unit cells and the exact relation of the parts of the molecule to each other must be partly in the nature of speculations. In the following discussion all available data have been called on to construct what appears to be rational conclusions concerning those questions of great theoretical chemical interest. These are to be considered as suggestions rather than as certain facts, pending exact assignment of coördinates for all the atoms within the unit cell.

The first conclusion to be drawn is that the two benzene rings in the diphenyl molecule are in prolongation of each other rather than doubled over on each other. This picture is one that is accepted by most organic chemists today and this serves as interesting confirmation. The evidence for this is that the molecule possesses a center of symmetry, a condition that could only be true for the prolongated molecule.

Secondly, the rings probably are not flat. In that case the molecule would be expected to have at least one plane of symmetry, and such is not present. Furthermore, assuming the molecules to be exactly in the *bc* plane, the intensities of successive order of the *h*00 planes would fall off regularly and such is not the case. Thus it is probable that the carbon atoms are in staggered or puckered rings, a conclusion which was reached by Hengstenberg and Mark. The 9.57 dimension may represent the length of the molecule, while the halvings of the 8.11 dimension show that two molecules share this length. Thus a single molecule might be considered to occupy a space approximately 4 X 5.7 X 9.5. It is probable that 5.7 is the width of the molecule, *i. e.*, the length in the meta direction of a benzene ring, and that the molecule is at a slight angle to the *c* axis in the *ac* plane, so that the actual thickness is less than 4.1 and the length greater than 9.5.

It is of interest to compare the unit cell dimensions for para benzene derivatives obtained by Dr. Caspari with the data for diphenyl derivatives. He recorded the following measurements.

	a	*b*	*c*	*n*
Quinol	13.24	5.20	8.11	4
p-Aminophenol	13.06	5.32	8.25	4
p-Phenylenediamine	12.46 × 2	5.93	8.29	8

The dimension of 5+ corresponding to the width of the ring checks with that obtained for diphenyl. The dimension 8–8.5 is also common to the diphenyl derivatives. Caspari suggests that it may correspond to the length of the molecule, while the hypothesis in this work is that it represents the thickness of two molecules and the longest dimension represents the length of two molecules. The halving of the **8.3** dimension in phenylenediamine as well as the space group involved suggests that the latter interpretation may be correct, although the evidence is not conclusive.

Hengstenberg and Mark obtained the following comparison for diphenyl, phenanthrene and fluorene.

	a	*b*	$c \sin \beta$
Diphenyl	8.22	5.69	**9.45**
Fluorene	8.48	**5.73**	**2 × 9.42**
Phenanthrene	**8.60**	**6.11**	**2 × 9.52**

. If the b axis represents the width, the *c* axis the length and the *a* axis the width of two molecules, the dimensions are very consistent with those obtained in the present work.

In the case of dimesityl and also of hexachlorodiphenyl, the molecule possesses no symmetry. This is of significance because the structural formulas of these two substances indicate the same symmetry that diphenyl itself possesses. The fact that such symmetry is missing leads to the conclusion that the two rings are either bent or turned at an angle to each other in these compounds. The other compounds exhibit asymmetry, as is to be expected from their formulas.

The spacings observed in the diagrams of dimesityl indicate that two molecules share the *c* axis and also the b axis, and that the molecule may extend with its length along the *c* axis, with a tilt of unknown amount. Thus the approximate volume occupied by one molecule might be 8.2 × 4.3 × **11.1.** The difference between **11.12** and.9.57 represents the difference between the space occupied by two methyl and two hydrogen groups together with the change in space caused by a distortion of the molecule as a whole or a change in tilt. Inasmuch as one-half of the difference, 0.8, is too small to account for the replacement of hydrogen by methyl alone, there must be a tilt or a compression of the molecule as a whole. The thickness of the molecule is slightly greater than that of diphenyl, while the width is increased by 2.55, a change which might be expected from the substitution of two hydrogens by two methyl groups.

The dimensions and intensities of reflection of 3,3-diaminodimesityl, both as the levo and dextro form, show that the structure is nearly identical with that of dimesityl, except for a very slight increase in the width of the molecule and in the length. This confirmed the expectation that the insertion of amino groups between the 2- and 4-substituted methyl groups would cause little change in the structure of the molecule as a whole. The similarity is interesting in view of the fact that although dimesityl cannot be resolved because the benzene rings are symmetrical, both compounds offer the same resistance to free rotation about the diphenyl linkage.

While hexachlorodiphenyl at first glance appears different from the others, its similarity becomes apparent when the *a* unit length is halved. Since all three of the spacings are halved, the domain of each molecule is approximately 7.9 X 4.3 X 10.74. This is exactly equal in thickness and shorter in both length and width than dimesityl. If it is assumed for the moment that the difference in width, $8.21 - 15.80/2 = 0.31$, represents the difference in space occupied by two methyl groups and two chlorine atoms, while the difference in length, $22.25 - 21.48 = 0.77$, accounts for the substitution of four methyl by four chlorine, the average difference between one methyl group and one chlorine atom would be 0.17.

The o-tolidine and the diphenic acid are not strictly comparable to the other compounds and were analyzed as incidental to **the** main problem. The dimensions of the o-tolidine indicate that it is similar in general structure to the other compounds. The unit c axis, 23.62, probably represents the length of two molecules, while 6.50 is reasonably the width of a molecule. The fact that the molecule would be longer than dimesityl and less thick than diphenyl indicates that this picture may not be correct in detail. However, this investigation was not pursued further, inasmuch as the compound bore little relation to the problem under investigation.

It is evident from the dimensions and also from the space group that diphenic acid crystallizes in a very different arrangement from that of the other compounds. The fact that carboxyl groups exert forces upon each other which result in a doubling of molecules has already been noted in the case of aliphatic long-chain compounds. It is probable that the presence of these polar groups distorts the diphenyl molecule into a very different orientation. It is certain .from the dimensions that the molecule cannot lie elongated along any of the axes and it is reasonable to suppose that the two rings are bent or turned at an angle to each other. The fact that this acid forms an anhydride readily would indicate that the two carboxyl groups are in close proximity. The solution of this problem, though interesting in itself, would shed no light on the question of stereoisomerism and therefore was not studied further.

The following premises have emerged from the above discussion as a basis for the complete picture of the positions of the molecules of diphenyl derivatives. The diphenyl molecule is symmetrical about a center; dimesityl and hexachlorodiphenyl have no symmetry. The molecules in all cases lie with their length parallel or at a slight tilt to the c axis. The rings of carbon atoms are in each case probably staggered and have a thickness which is constantly 4.3 for the derivatives and 4.1 for diphenyl itself. The width across the ring is 5.6 for diphenyl, 7.9 for hexachlorodiphenyl and 8.1 for dimesityl and its diamino derivative. The respective lengths of these compounds are 0.5, 10.75, 11.1 and 11.3.

Discounting the staggering for the moment, there are the possibilities that the two rings may lie in the same plane, in planes at small angles to each other, or at right angles. The space considerations do not favor the first. The facts that the molecules are asymmetric and that they occupy the spaces given in the preceding paragraph lead to the conclusion that the two rings are in planes turned from each other at an angle of not greater than 45° in the 2,2′,6,6′-derivatives of diphenyl, while the rings in diphenyl itself are coplanar.

Summary

1. Unique solutions of the crystal structure for diphenyl and five of its derivatives have been determined by rotating and oscillating crystal methods.
2. The possible size, shape and position of the molecules of these compounds are discussed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OR KITASATO INSTITUTE]

SYNTHESIS OF QUINOLINE COMPOUNDS. VI. PREPARATION OF CERTAIN ACYLAMINO DERIVATIVES OF 8-HYDROXYQUINOLINE

BY KONOMU MATSUMURA AND CHUSABURO SONE

RECEIVED JULY 17, 1930 PUBLISHED JANUARY 12, 1931

The acyl derivatives of aminohydroxyquinoline described in this paper were prepared in connection with a study of the bactericidal action of quinoline compounds.

Experimental

The aminohydroxyquinoline (1 mole) and acetic anhydride (1.1 moles) were allowed to react in ether solution for three days at room temperature in the presence of finely ground sodium acetate, with occasional stirring. The ether was then evaporated and sufficient water was added to dissolve the sodium acetate. The product was filtered, washed and finally recrystallized. The yields were very good.

In general, these quinoline derivatives are sparingly soluble in water and ether, fairly soluble in benzene and very soluble in alcohol and chloroform. Their salts with mineral acids can be crystallized from alcohol and they are all soluble in water except the hydrochloride of 7-iodo-5-acetamino-8-hydroxyquinoline, which undergoes hydrolysis with separation of free base.

TABLE I

HYDROXYQUINOLINE DERIVATIVES

No.	Quinoline derivative	Form	Solvent	M. p., °C.
1	7-Iodo-5-acetamino-8-hydroxy-	Colorless needles	EtOH	212
2	5-Acetamino-8-hydroxy-	Colorless prisms	$CHCl_3$	218–219
3	5-Acetamino-6-hydroxy-	Colorless needles	EtOH	278 (dec.)
4	7-Acetamino-5-methyl-8-hydroxy-	Pale yellow prisms	EtOH	203–204
5	7-Acetamino-5-methyl-8-acetoxy-	Colorless columns	C_6H_6	222
6	5-Methyl-8-methoxy-[a]	Viscous yellow oil	B. p. 298–302	(773 mm.)
7	7-Amino-5-methyl-8-hydroxy-[d]	Yellow prisms	Ether	141–142
8	5-Benzoylamino-8-hydroxy-[e]	Colorless plates	EtOH	237–238
9	7-Benzoylamino-5-methyl-8-benzoyloxy-[f]	Colorless columns	C_6H_6	181

No.	Formula	Analyses, % Calcd.	Analyses, % Found	Name	Salt form	M. p., °C.
1	$C_{11}H_9O_2N_2I$	N, 8.54	8.23	Hydrochloride	Yellow needles	196 (dec.)
2	$C_{11}H_{10}O_2N_2$	N, 13.86	13.69	Acid sulfate	Yellow needles	263 (dec.)
3	$C_{11}H_{10}O_2N_2$	N, 13.86	13.54	Acid sulfate	Colorless columns	...
4	$C_{12}H_{12}O_2N_2$	N, 12.96	13.00	Neut. sulfate	Yellow needles	180
5	$C_{14}H_{14}O_3N_2$	N, 10.85	11.02	Acid sulfate	Yellow plates	183
6	$C_{11}H_{11}ON$	....	...	Picrate[b]	Yellow needles from alc.	180–181
				Chloroplatinate[4]	Yellow prisms	224 (dec.)
7	$C_{10}H_{10}ON_2$	C, 68.97 H, 5.75 N, 16.09	68.90 5.56 16.11	Picrate	Red needles from EtOH; dec. at 215–220° without melting	
8	$C_{16}H_{12}O_2N_2$	N, 10.60	10.57	Acid sulfate	Yellow needles from EtOH	225–227 (dec.)
9	$C_{24}H_{18}O_3N_2$	C, 75.39 H, 4.71 N, 7.33	75.54 4.83 7.26	....	....	...

[a] Made by refluxing a methyl alcohol solution (30 cc.) of 5-methyl-8-hydroxyquinoline (15.9 g.) with methyl iodide (14.2 g.) and potassium hydroxide (5.6 g). [b] Calcd. for $C_{11}H_{11}ON \cdot C_6H_3O_7N_3$: C, 50.75; H, 3.48; N, 13.93. Found: C, 50.89; H, 3.74; N, 14.17. [c] Calcd. for $(C_{11}H_{11}ON \cdot HCl)_2PtCl_4$: C, 34.92; H, 3.17; Pt, 25.82. Found: C, 34.68; H, 3.24; Pt, 25.78. [d] Prepared by reduction of 7-nitroso-5-methyl-8-hydroxyquinoline (4.2 g.) in glacial acetic acid (60 *g.)* by means of stannous chloride (12 *g.)* in concentrated hydrochloric acid (42 cc.); cf. Ganelin and Kostanecki, *Ber.*, 24, 3979 (1891). [e] Obtained in 91% yield by interaction of equimolecular amounts of 5-amino-8-hydroxyquinoline and benzoyl chloride in cold pyridine solution. [f] Prepared from **7-amino-5-methyl-8-hydroxyquinoline** and benzoyl chloride in ether solution (at room temperature) in the presence of sodium acetate.

I desire to express my hearty thanks to Professor Hata for the interest which he has kindly taken in this work.

Summary

5-Acetamino-6-hydroxy-, 5-acetamino-S-hydroxy-, 7-iodo-5-acetamino-8-hydroxy- and 7-acetamino-5-methyl-8-hydroxyquinoline have been prepared and characterized.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE REDUCTION OF NAPHTHALENE BY ALKALI METALS IN LIQUID AMMONIA[1]

BY CHARLES BUSHNELL WOOSTER AND FRANK B. SMITH

RECEIVED JULY 26, 1930 PUBLISHED JANUARY 12, 1931

The reaction between sodium and naphthalene in liquid ammonia solution was first investigated by Lebeau and Picon[2] and the products which they obtained at 15° were sodium amide and tetrahydronaphthalene. These facts are equally open to two different interpretations.

I. It may be assumed that the naphthalene was reduced by nascent hydrogen generated by a reaction between the alkali metal and the solvent.

$$4Na + 4NH_3 \longrightarrow 4NaNH_2 + 4(H) \qquad (1)$$

$$4(H) + C_{10}H_8 \longrightarrow C_{10}H_{12} \qquad (2)$$

This hypothesis is analogous to that advanced by Kekulé, Kolbe, von Baeyer and others[3] to explain reductions of organic substances with sodium amalgam and water.

II. The formation of tetrahydronaphthalene may also be attributed to a solvolytic action of the solvent upon an organo-alkali compound which was formed as an intermediate product.

$$C_{10}H_8 + 4Na \longrightarrow C_{10}H_8Na_4 \qquad (3)$$

$$C_{10}H_8Na_4 + 4NH_3 \longrightarrow C_{10}H_{12} + 4NaNH_2 \qquad (4)$$

This assumption is analogous to an alternative theory of amalgam reduction recently proposed by Willstatter, Seitz and Bumm.[4]

This reaction, therefore, is of especial interest as a test case for indicating the possibilities of wider application of the two general hypotheses.

Dipotassium[5] and dilithium[6] derivatives of naphthalene have been pre-

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[1] Paper presented at the Cincinnati meeting of the American Chemical Society, September, 1930.

[2] Lebeau and Picon, *Compt. rend.*, 158, 1514 (1914).

[3] (a) Kekulé, *Ann. Suppl.*, 1, 129 (1861); (b) Herrmann, *Ann.*, 132, 75 (1864) (an account of work done in Kolbe's laboratory); (c) von Baeyer, *ibid.*, 269, 145, 170, 174 (1892).

[4] Willstatter, Seitz and Bumm, *Ber.*, 61,871 (1928).

[5] Berthelot, *Ann.*, 143, 98 (1867); *Ann. Suppl.*, 5, 370 (1867); *Ann. chim.*, [4] 12, 157, 205 (1867)

[6] Schlenk and Bergmann, *Ann.*, 463, **83** (1928).

pared by the action of alkali metals on the pure hydrocarbon at elevated temperatures and on its solutions in organic solvents at room temperature, respectively, but thus far no similar derivatives containing a higher proportion of alkali metal have been reported. Preliminary observations indicated the formation of a compound between potassium and the hydrocarbon in liquid ammonia at lower temperatures, and, accordingly, a more detailed study of the reaction under these conditions was undertaken.

Experimental Part

Ratio of Sodium and Potassium to Naphthalene.—It is an evident consequence of the second hypothesis outlined above that the maximum amount of sodium entering into reaction must bear a definite relation to the quantity of naphthalene used, whereas no such restriction is demanded by the first hypothesis. In attempting to determine the number of sodium atoms which react with a molecule of naphthalene, considerable experimental difficulties were encountered. It was equally difficult to titrate a known amount of sodium with naphthalene or a known amount of naphthalene with sodium because the reaction does not go to completion with ease. If an excess of sodium were used, titration with ammonium bromide to the disappearance of the blue color of the free metal would lead to erroneous results, since ammonium bromide would also react with a sodium compound of naphthalene. Advantage was taken of the fact that ammonium bromide reacts with free sodium to liberate hydrogen, whereas no hydrogen would be formed in its reaction with a sodium compound of naphthalene. This method was open to a possible source of error, since the hydrogen evolved might itself react with naphthalene or its reduction products, thus making the apparent sodium ratio too high. If ethyl bromide were used instead, the ethane evolved would not react with naphthalene or its reduction products, but the reaction between ethyl bromide and the organo-alkali compound might also generate gaseous products and indicate too low a sodium ratio.[7] However, if the same value were obtained by both methods, it would seem reasonable to suppose that these possible sources of error are merely hypothetical.

The apparatus employed was similar to that previously described.[8] It was found necessary, however, to alter the design of the reaction tube in order to promote complete reaction. The gaseous ammonia was admitted through an inlet at the very bottom of

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[7] Another possibility requiring consideration is that of gas formation between ethyl bromide and the sodium amide resulting from Reaction 1 or 4. However, ethyl bromide reacts but slowly with sodium amide in liquid ammonia at −40° and even in the more rapid reaction at room temperature, only small amounts of ethylene are formed [Picon, Bull. *soc. chim.*, 35, 979–81 (1924)] It may be expected, therefore, that ethylene would not be evolved in quantities too large to be removed by solution in the water over which the gases were collected.

[8] Wooster, THIS JOURNAL, 51, 1859 (1929).

the reaction tube to insure vigorous stirring and the top of the reaction tube was fitted with a ground-in dropping funnel which permitted liquids or solutions to drip directly into the agitated reaction mixture.

The sodium was cut under petroleum ether, weighed under "Nujol," washed with petroleum ether, placed in the bottom of the reaction tube and ammonia condensed upon it A suitable amount of pure, dry naphthalene was dissolved in a small quantity of dry toluene and the solution added slowly with vigorous stirring to the sodium solution after which the reaction mixture was stirred slowly with a stream of ammonia gas for a period of several hours. In Experiments 1 and 2, dry ammonium bromide was then added and the evolved gas collected over water. The greenish color of the reaction mixture was slowly discharged and gave way to a bright transparent red, after which no more gas was evolved upon further addition of ammonium bromide, although the red color eventually disappeared. The collected gas was dried and characterized by its density as hydrogen. In Experiments **3** and 4, pure, dry ethyl bromide was used instead of ammonium bromide to dissipate the free sodium. The procedure and observations were analogous to those just described except that the gas collected was found by its density to be ethane. In experiments using potassium instead of sodium, it was found that the amount of gas liberated by the action of ammonium bromide depended somewhat on the length of time the reaction was allowed to proceed. If sufficient time elapsed, the reaction mixture eventually turned red before ammonium bromide was added, and the action of this reagent did not result in the formation of any gas. This behavior is apparently due to a slow ammonolysis of the excess potassium, since hydrogen is evolved during the process. In Experiments 5 and 6 no ammonium bromide was added and hydrogen was collected from the very beginning of the reaction until the red color appeared, when the evolution of gas ceased. The results of these experiments appear in Table **I**.

TABLE I

RATIO OF SODIUM AND POTASSIUM TO NAPHTHALENE

No.	Metal, g.	$C_{10}H_8$, g.	Gas, cc.	Na or K consumed, atoms/mole of $C_{10}H_8$
1	0.4585 (Na)	0.5609	35.65 (H_2)	3.83
2	2.6411 (Na)	2.9468	315.1 (H_2)	3.77
3	2.0620 (Na)	2.3040	181.0 (C_2H_6)	4.09
4	1.6240 (Na)	1.6628	204.1 (C_2H_6)	4.04
5	1.6158 (K)	1.0037	128.4 (H_2)	3.81
6	1.4161 (K)	0.9021	114.4 (H_2)	3.70

It seems evident from the first four values in column five that only four atoms of sodium per molecule of naphthalene react regardless of the quantity of excess metal present and (within reasonable limits) of the time elapsed, the somewhat low values obtained in the first two experiments being doubtless due to the presence of small amounts of hydrogen in the ammonia, incident to the previous drying of this solvent with sodium. This is decidedly in favor of the second mechanism, outlined in the introduction, and it may be concluded that the four sodium atoms primarily add to a molecule of naphthalene.

The last two values in column five indicate that approximately four equivalents of potassium per mole of naphthalene reacted without the formation of gaseous products. Although in this case the gradual ammonolysis of the potassium[9] prevents a discrimination between the two mechanisms on the basis of the quantitative results, the formation of the characteristic transparent red solution strongly suggests the presence of an organo-alkali compound.

Identification of the Product of Hydrolysis of the Sodium Derivative.—Although the evidence presented above indicates that four atoms of sodium react with each molecule of naphthalene, it does not indicate which positions the sodium atoms enter. Accordingly, the hydrolysis product of the sodium compound was prepared and its properties studied for the purpose of identification.

Twenty-three grams of sodium was dissolved in liquid ammonia in a large Dewar flask equipped with a mechanical stirrer;[10] 30 g. of naphthalene, or slightly less than one molecule to every four atoms of sodium, was then added slowly in ether solution and the reaction mixture stirred for twenty-four hours. Ammonium bromide was added in excess and after the ammonia had been allowed to evaporate, the Dewar flask was washed out with water. The oil which separated was taken up in ether and the aqueous solution extracted with this solvent. The combined ethereal extracts were dried over sodium hydroxide and evaporated on a water-bath leaving a yellow oil which was carefully distilled *in vecuo.* A colorless, highly refractive oil boiling at 50–55° under less than 1 mm. pressure constituted the main reaction product. This substance did not react with solutions of bromine in carbon tetrachloride at room temperature and the reaction which occurred upon heating with liquid bromine was accompanied by the evolution of hydrobromic acid. These facts distinguish the product from the dihydronaphthalenes and, accordingly, it was compared with a carefully distilled sample of commercial tetralin. Both substances, independently and when mixed, boiled at 207–207.5" under 753 mm., and the density of both was 0.965 ± 0.0005 at 25°. Since tetralin has been demonstrated to be 1,2,3,4-tetrahydronaphthalene,[11] the four sodium atoms must add in the 1,2,3,4 positions.

Observations Indicating Ammonolysis.—When the residue from the evaporation of ammonia from the sodium and naphthalene reaction mixture was heated by surrounding the evacuated reaction tube with a steam jacket, a liquid distilled and collected in drops on the cool upper walls of the tube. This circumstance indicates the formation of tetrahydronaphthalene by ammonolysis at higher temperatures and accounts for the fact that Lebeau and Picon were able to obtain this substance directly from the interaction of sodium and naphthalene.

It remained to be determined whether in liquid ammonia at its boiling point the tetrasodium tetrahydronaphthalene was entirely stable or whether it was partly ammonolyzed. The following observation suggested the latter to be the case. When oxygen was passed through the reaction mixture the presence of nitrite ions in the residue could be shown by a qualitative test with potassium iodide, hydrochloric acid and carbon

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[9] This action may well be ascribed to the catalytic influence of the potassium amide formed in the ammonolysis of the potassium compound of naphthalene [unpublished observations of one of the authors (C. B. W.)]. Sodium amide exerts a similar influence upon the ammonolysis of sodium [Kraus, THIS JOURNAL, 29, 1569 (1907)], but this reaction is too slow to interfere with the experiments described.

[10] This apparatus has been previously described [Wooster and Mitchell, *ibid.*, 52, 691 (1930)].

[11] Schroeter, *Ann.*, 426, 83 (1922).

disulfide. This proves the presence of sodium amide in the original solution since it is oxidized under these conditions with formation of sodium nitrite.[12]

Quantitative Study of the Ammonolysis.—Although it is true that the occurrence of ammonolysis would result in an increase in weight of the reaction residue, this fact does not serve as a basis for a suitable method of attacking the problem under consideration. Apart from the errors introduced by the volatility of the products, it is evident that the increase in weight exhibited by the contents of a reaction tube which has been evacuated after it has attained room temperature will be determined by the state of equilibrium characteristic of the residue at room temperature and not of the solution in liquid ammonia at its boiling point. If, on the other hand, the tube is evacuated at the temperature of boiling ammonia, the equilibrium may be displaced during the evaporation of the solvent and the result may also be influenced by the weight of solvent retained as ammonia of crystallization.

Consequently, a method of analysis was sought which could be applied directly to the liquid ammonia solutions. No such method was found which was capable of precision, but a procedure was developed which provided approximate values of the degree of ammonolysis. This procedure was based upon a study of the products formed in oxidizing the reaction mixture. Rengade,[12] by leading oxygen into solutions of cesium, potassium and sodium amides in liquid ammonia, found oxidation to take place according to the equation,

$$2MNH_2 + 1^1/_2O_2 = MOH + MNO_2 + NH_3$$
$$(M = Cs, K \text{ or } Na) \qquad (5)$$

The oxidation of metallic sodium in liquid ammonia yields the peroxide, Na_2O_2.[13]

According to Kraus and Rosen[14] sodium peroxide and triphenylmethyl peroxide may be obtained by the oxidation of sodium triphenylmethide in liquid ammonia. It is reasonable to suppose that the sodium or potassium in combination with naphthalene would also be oxidized to the peroxide. Thus if a reaction mixture contained sodium amide, a sodium hydronaphthalene and free sodium, the inorganic oxidation products should be sodium nitrite, sodium hydroxide and sodium peroxide. Since the oxidation of the materials in solution is reasonably rapid, and since both the organo-alkali compound and the alkali metal amide are simultaneously attacked and destroyed, displacement of the ammonolytic equilibrium would be minimized, and it might be expected that a determination of the amounts of nitrite and peroxide formed would furnish an approximate estimate of the degree of ammonolysis.

[12] Rengade, *Ann. chim. phys.*, 11, 348 (1907).

[13] Kraus and Whyte, THIS JOURNAL, 48,1781 (1926).

[14] Kraus and Rosen, *ibid.*, 47, 2739 (1925).

The sodium peroxide was separated from sodium nitrite by treating the ice-cold aqueous solution of the residue left after oxidation and subsequent evaporation of the ammonia, with an ice-cold solution of barium chloride, as described by Schrader.[15] The precipitate of barium peroxide was separated by filtration, washed, dried and analyzed. The filtrate was then analyzed for nitrite ions.

The method of nitrite analysis used was that developed by Gerlinger,[16] in which the nitrite solution is boiled with a concentrated solution of ammonium chloride in an atmosphere of carbon dioxide, and the nitrogen evolved is collected over potassium hydroxide solution. The amount of nitrite is calculated from the amount of nitrogen liberated, according to the equation

$$NH_4Cl + MNO_2 \longrightarrow MCl + 2H_2O + N_2 \qquad (6)$$

A method of peroxide determination was developed in which the solid barium peroxide was added to a strong solution of potassium iodide, strong hydrochloric acid added, and the liberated iodine titrated with standard thiosulfate solution. Calculations were based on the equation

$$BaO_2 + 4HCl + 2KI + 2Na_2S_2O_3 \longrightarrow 2H_2O + BaCl_2 + 2KCl + 2NaI + Na_2S_4O_6 \qquad (7)$$

In order to determine how nearly quantitatively potassium and sodium amides were oxidized under the conditions of the experiments, potassium was converted to the amide, oxidized and the products analyzed. Sodium was converted partially to the amide, the mixture of amide and free metal oxidized and the products analyzed. (The extent of the ammonolysis was in each case determined by collecting the hydrogen formed.) The results are indicated in Table II, where all amounts are given in milliatoms or millimoles.

TABLE II

OXIDATION OF SODIUM AND POTASSIUM AMIDES

No.	Metal	Amount	Amide formed	Nitrite Found	Nitrite Calcd.	Peroxide Found	Peroxide Calcd.
1	Potassium	26.5	25.6	10.6	12 8	None	None
2	Potassium	31.3	303	128	15.2	None	None
3	Sodium	47.7	30.2	12.0	15.1	0.1	17.5

In the following experiments a slight excess over four atoms of alkali metal was allowed to react with each molecule of naphthalene. In the case of potassium, the excess metal was converted to the amide before oxidation. Excess sodium was left as free metal before oxidation. The results of several experiments are summarized in Tables III and IV, where all corrected values are calculated by the use of the data in Table II. All quantities are given in milliatoms or millimoles.

The corrected amount of sodium amide formed by ammonolysis of the organo-alkali compound is given in column six. In the experiment re-

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[15] Schrader, *Z. anorg. Chem.*, 108, 44 (1919).

[16] Gerlinger, *Z. angew. Chem.*, 50, 1250 (1901).

TABLE III

OXIDATION OF SODIUM COMPOUND, FREE SODIUM AND SODIUM AMIDE

No.	Sodium	$C_{10}H_8$	Nitrite	Amide Found	Amide Corr.	Peroxide	Free metal	Sodium compound
1	43.06	1007	12.40	24.92	31.15	9.05	278	9.03
2	57.23	14.00	17.82	35.64	44.05	9.89	1.23	9.35

corded in Table II very little peroxide was obtained from the oxidation of the free metal; accordingly the major portion of the peroxide obtained in these oxidations was ascribed to the oxidation of the organo-alkali compound, as may be seen upon examination of column nine. The results indicate that of the four sodium atoms which are known to react with naphthalene, **3.09** and **3.15** are converted into sodium amide by the solvent while **0.90** and 0.67 atoms appear definitely to remain in combination with the naphthalene.

TABLE IV

OXIDATION OF POTASSIUM COMPOUND AND POTASSIUM AMIDE

				Amide				
No.	Potassium	$C_{10}H_8$	Nitrite	Found	Corr.	From excess	From ammonolysis	Peroxide
1	27.4	6.5	7.9	15.8	18.8	1.4	17.4	0.4
2	27.1	6.5	8.4	16.6	19.8	1.1	18.7	.5

The values in column eight represent the amounts of potassium amide presumably resulting from ammonolysis of tetrapotassium tetrahydronaphthalene. They correspond to 2.68 and **3.04** molecules per molecule of naphthalene, respectively. As no free metal was present during the oxidation in these experiments, the peroxide[17] could only result from the oxidation of an organo-alkali compound. Thus the existence of peroxide in the oxidation products together with the observation of the characteristic red color, previously noted, constitute definite evidence of the presence of an organo-alkali compound in the reaction mixture. Furthermore, the approximate correspondence between the results given in Tables III and IV indicates that the reaction between potassium and naphthalene is not essentially different from that which takes place when sodium is used.

Discussion

The evidence presented in this paper shows that the reduction of naphthalene with sodium in liquid ammonia takes place through the intermediate formation of a 1,2,3,4-tetrasodium addition product which is

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[17] The low values for the peroxide given in the table may to a large extent be ascribed to the fact that potassium peroxide is capable of further oxidation under the conditions of these experiments and that the higher oxides so formed might escape notice in the analytical procedure employed. In contrast to these low peroxide values, but in agreement with the amounts of amide formed, the general behavior of alkali metal amides in liquid ammonia suggests that the potassium compounds would be less susceptible to ammonolysis than the corresponding sodium compounds.

approximately three-fourths ammonolyzed even in solution at $-33.5°$. This confirms the mechanism derived by an extension to this case of the theory proposed by Willstatter, Seitz and Bumm[4] to explain amalgam reductions.

It is of interest to note that of the compounds which were also found by Lebeau and Picon[18] to be reduced to hydro derivatives with formation of sodium amide: anthracene,[19] phenanthrene, biphenyl,[20] stilbene and phenylethylene[21] have been found to yield addition products with the alkali metals or with organo-alkali compounds, whereas the compounds which failed to undergo such a reduction (amylene, benzene, toluene, cymene, terpinene, terpinoline, carvene, terebene, a-pinene and menthene) have not as yet been found capable of adding the alkali metals, although several have been specially investigated with this point in view.[22] This coincidence cannot fail to suggest that these other reductions observed by Lebeau and Picon proceed by means of a mechanism similar to that just demonstrated to operate in the reduction of naphthalene.

It is perhaps also worth mention that whereas catalytic reduction of naphthalene always yields a tetrahydro or more highly hydrogenated derivative,[23] the reducing action of sodium in alcohol[24] may also yield a dihydro derivative in which the additional hydrogen atoms occupy the same positions (1,4) as do the alkali metal atoms in the dilithium and dipotassium addition products which have been prepared. Here again the postulate of an intermediate organo-alkali compound in the reduction process is in harmony with the evidence available.

Summary

1. It has been shown that the reduction of naphthalene with sodium in liquid ammonia takes place through the intermediate formation of a 1,2,3,4-tetrasodium addition product, which is approximately three-fourths ammonolyzed even in solution at $-33.5°$.

2. The reaction with potassium apparently follows essentially the same course as that with sodium.

3. These facts confirm the mechanism derived by extending to this reaction the theory proposed by Willstatter, Seitz and Bumm to explain reductions of organic compounds with sodium amalgam and water.

4. Certain facts have been pointed out which suggest a similar mecha-

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[18] Lebeau and Picon, *Compt. rend.*, 157, 223 (1913); *ibid.*, **159**, 70 (1914).

[19] Schlenk and Bergmann, *Ann.*, 463, 98–227 (1928).

[20] Schlenk and Bergmann, *ibid.*, 463, 2–97 (1928).

[21] Ziegler, Crossmann, Kleiner and Schäfer, *ibid.*, 473, 1 (1929).

[22] Unpublished observations of one of the authors (C. B. W.).

[23] (a) Leroux, *Compt. rend.* 139, 673 (1904); *Ann. chim.*, [8] 21, 465, 466 (1910). (b) Sabatier and Senderens, *Compt. rend.*, 132, 1257 (1901).

[24] Bamberger and Lodter, *Ber.*, 20, 1703 (1887).

nism for the reduction of other aromatic compounds by sodium in liquid ammonia and for the reduction of naphthalene by sodium in ethyl alcohol.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

SYNTHESIS OF SOME NEW COMPOUNDS IN THE PYRROLE AND PYRROLIDINE SERIES

BY LYMAN C. CRAIG WITH R. M. HIXON

RECEIVED JULY 28, 1930 PUBLISHED JANUARY 12, 1931

A previous paper[1] reported the preparation of pyrrolidine, N-phenylpyrrolidine and N-cyclohexylpyrrolidine. In extending the series for the contemplated study of insecticidal action and physical properties, the benzyl, methyl, butyl and *p*-tolyl derivatives were desired.

The aliphatic N-substituted derivatives can be prepared by the general method of Britton[2] or by addition of RX to the free base. Contrary to the literature[3] the yield by the latter method is low due to the formation of the quaternary derivative. The general method to be recommended for the preparation of N-substituted derivatives where R is a saturated aliphatic radical is to prepare the N-substituted pyrrole and reduce it catalytically as pyrrole was reduced. The presence of excess acid is necessary for a successful reduction. Substitution on the nitrogen appears to stabilize the ring toward polymerization by acid, eliminating the difficulty encountered with the carbon substituted derivatives.[4] J. P. Wibaut[5] reduced methylpyrrole catalytically with Adams and Shriner catalyst in glacial acetic acid, but his reduction required large amounts of catalyst and shaking for a long period of time. If alcohol acidified with hydrochloric acid is used as a solvent, the reduction requires only 0.2 g. of catalyst and is complete in three hours. The same catalyst may be used several times. N-Methylpyrrole has also been reduced successfully to N-methylpyrrolidine by passing its vapor over palladium[6] at 160°.

Tadeus Reichstein[7] gave a method for the characterization of N-substituted pyrroles by the use of a diazo reaction. Reduction can also be used for this purpose since the yield is practically quantitative and the resulting pyrrolidine derivative can easily be identified as the picrate.

In the N-butylpyrrole synthesis the formation of the substituted acid

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[1] Craig and Hixon, THIS JOURNAL, 52, 804 (1930).

[2] E. C. Britton, U. S. Patent 1,607,605, Nov. 23, 1926.

[3] Schlinck, *Ber.*, 32, 952 (1899); Ciamician and Magnaghi, *ibid.*, 18, 2079 (1885).

[4] Anderson and McElvain, THIS JOURNAL, 51, 887 (1929).

[5] Wibaut, *Rec. trav. chim.*, 44, 1101–5 (1925); Dejong and Wibaut, ibid., 49, 237 (1930).

[6] Zelinsky and Jerjew, *Ber.*, 62, 2589 (1929).

[7] Reichstein, Helv. *Chim. Acta*, 10, 387 (1927).

amide is greater than with the N-methylpyrrole or pyrrole synthesis. By the use of reduced pressure in the distillation of the mucic acid salt, the yield of butylpyrrole was practically doubled.

p-Toluidine condenses smoothly with tetramethylene chloride to give satisfactory yields of N-p-tolylpyrrolidine.

Experimental

N-Normal-butylpyrrole.—The method of preparation was that of Reichstein except that mucic acid was used instead of saccharic. To 86 g. of mucic acid in enough water to make a thin paste, 60 g. of butylamine was added. Upon cooling the reaction mixture solidified. It was transferred to a 500-cc. Claisen flask and subjected to distillation under reduced pressure (35 mm.). The distillate contained 35 g. of an oil which was extracted with ether, dried and fractionated, giving 13.5 g. distilling at a temperature of 165–180°. This was used for reduction. It was a colorless oil and had a very disagreeable sharp odor.

N-Butylpyrrole-a-carboxy-normal-butylamide.—The high-boiling residue (21.5 g.) from above was subjected to distillation under reduced pressure (165–170° under 10–12 mm. pressure). The colorless distillate solidified. It melted at 57° and crystallized in needles from an alcohol–water mixture.*

An attempt to hydrolyze the substituted acid amide by refluxing over strong caustic was unsuccessful, as was also an attempt using alcoholic potash at 130°. The compound was finally hydrolyzed by heating for ten hours at 200°, 10 g. of the amide in an alcoholic solution containing 8 g. of potassium hydroxide in 4 cc. of 95% alcohol. After hydrolyzing, most of the alcohol was distilled off and water added to the residue. Fractionation of this mixture by solubility in ether, acid solution and basic solution yielded about 1 g. of unchanged amide, N-butylamine and an acid fraction. The oily acid fraction, which was N-butylpyrrole-a-carboxylic acid, was finally characterized by conversion to the acid amide. It is soluble in all organic solvents and insoluble in water. The calcium, barium and silver salts were too soluble to crystallize. Six grams of the free acid was subjected to distillation under 6 mm. pressure. From the distillate three grams of an alkali-insoluble oil was obtained that distilled at 165 to 178° and had all the characteristics of N-butylpyrrole. Two grams of the original acid was present in the distillate. Evidently carbon dioxide splits off quite readily from this acid.

N-Butylpyrrole-a-acid Amide.—To 1 cc. of the free acid an excess of thionyl chloride was added. After heating, as much of the excess thionyl chloride was evaporated as was possible using reduced pressure and heating on the water-bath. The residue was dropped into cold concentrated ammonia and the resulting oily mass extracted with ether. The ether extract was evaporated to dryness and the residue recrystallized from hot water. The yield is low; m. p. 108°.

Anal. Calcd. for $C_9H_{19}N_2O$: C, 64.9; H, 8.99. Found: C, 64.98, 65.00; H, 8.52, 8.88.

Reduction of N-Methylpyrrole and N-Butylpyrrole.—The N-methylpyrrole was prepared by the method of Bell and Lapper.[9] To 10 cc. of pyrrole base in 100 cc. of absolute alcohol, 0.2 g. of Adams and Shriner catalyst and an equivalent of hydrochloric acid were added. In three hours in the case of N-methylpyrrole and five hours in the case of N-butylpyrrole the reduction was complete. The catalyst was filtered off and

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[8] Reichstein reported a compound, which corresponded to the above, as N-butylpyrrole-a-isobutylamide. This must be a typographical error, since normal-butylamine was used in the synthesis of his compound.

[9] Bell and Lapper, *Ber.*, 10, 1861 (1877).

the alcohol removed by distillation. The residue was washed with ether and treated with solid potassium hydroxide until an oil separated. The oil was dried over solid potassium hydroxide and distilled, The N-methylpyrrolidine distilled entirely at 76–78°, the yirld being almost the theoretical. N-Methylpyrrolidine has a stifling odor and a very high vapor pressure at room temperature. Its vapor pressure is 99 mm. at 25°. This may account for the emphasis in the literature placed on its physiological properties.

The yield of N-butylpyrrolidine is 88% of the theoretical. It is slightly soluble in water and has an odor similar to pyrrolidine. The picrate crystallized in leaflets from 95% alcohol and showed a constant melting point of 124°. An attempt was made to prepare a chloroplatinate by addition of a solution of chloroplatinic acid to the hydrochloride of the free base but the salt appeared to be too soluble to crystallize. A chloroaurate was prepared by this method using chloro-auric acid. It was very soluble in alcohol but crystallized in yellow leaflets from hot water. It melted without decomposition at 78°.

Anal. Calcd. for $C_8H_{17}NHAuCl_4$: Au, 42.13. Found: Au, 42.14, 42.08.

N-*p*-Tolylpyrrolidine.—To 5 g. of tetramethylene chloride[10] (boiling point 154–164°) 12.6 g. of p-toluidine was added. Upon heating on a steam-bath for ten hours, it formed a solid mass of crystals that entirely dissolved in dilute hydrochloric acid. The acid solution was washed with ether, made strongly alkaline and the oily layer run through a primary–secondary–tertiary amine separation with benzenesulfonyl chloride. A yield of 4.5 g. of a tertiary amine was obtained. It was dried over solid potassium hydroxide and distilled at a constant temperature of 120° under 8 mm. pressure. It crystallized in leaflets from an alcohol–water mixture and showed a constant melting point of 42.5°. It has a rather pleasant odor

A chloroplatinate was prepared in the usual way but it could only be recrystallized from water containing considerable hydrochloric acid, as reduction took place in water alone. It showed a decomposition point of 175°. For analysis the material was recrystallized and dried at room temperature in a vacuum desiccator.

Anal. Calcd. for $(C_{11}H_{15}N)_2H_2PtCl_6$: Pt, 26.68. Found: Pt, 26.70, 26.67.

N-Benzylpyrrolidine.—This compound was first prepared by Schlinck.[11] He reported a nearly quantitative yield which could not be duplicated by the same method. To 5 cc. of pyrrolidine,[12] one-half equivalent of benzyl chloride was added (a full equivalent gave a lower yield of N-benzylpyrrolidine than a half). The mixture was warmed for two hours on a water-bath. Dilute hydrochloric acid was added and the unreacted halide removed by washing with ether. Upon addition of caustic solution, an oil separated; when solid potassium hydroxide was added, a third layer appeared. The top layer was drawn off and identified as N-benzylpyrrolidine. It amounted to 4 g. or a yield of 40% of the theoretical. Its picrate melted at 128° as reported by Schlinck.

The second layer (the larger) was viscous, insoluble in ether, very soluble in water and required a concentrated solution of potassium hydroxide to make it separate. It could not be prepared in a form suitable for analysis but its properties are what would be expected of dibenzylpyrrolidinium hydroxide.

Summary

It has been shown that the N-substituted pyrroles can be reduced easily to the corresponding pyrrolidine compounds in alcohol–hydrochloric acid

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[10] Prepared from pprolidine by the method of Braun and Beschke, ***Ber.*, 39,** 4119 (1906).

[11] Schlinck, *Ber.*, 32, 952 (1899).

[12] Obtained by catalytic reduction of pyrrole.

solution. This method of preparation is to be preferred over that of condensation of RX with pyrrolidine as the yields are often low by the latter method due to formation of the quaternary derivative.

p-Toluidine condenses smoothly with tetramethylene chloride to give N-*p*-tolylpyrrolidine.

The compounds N-*p*-tolylpyrrolidine, N-n-butylpyrrole-a-carboxylic acid' and N-n-butylpyrrole-a-acid amide are reported for the first time. The properties of N-n-butylpyrrolidine, N-n-butylpyrrole and N-*n*-butylpyrrole-a-carboxy-N-butyl amide are given.

AMES, IOWA

[CONTRIBUTION NO. 36 OF THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

THE CATALYTIC EFFECT OF MAGNESIUM ALCOHOLATES ON THE REACTION OF GRIGNARD REAGENTS WITH CARBON DIOXIDE[1]

BY CORLISS R. KINNEY AND M. L. MAYHUE

RECEIVED AUGUST 12, 1930 PUBLISHED JANUARY 12, 1931

Although many substances have been shown to have deleterious effects in Grignard reactions, nothing appears to be known about the effect of alcohols, which are often present in the organo halides from which the reagents are made. The catalytic behavior of alcohols or their magnesium derivatives was first brought to our attention by the variable yield of triphenylacetic acid obtained from triphenylmethylmagnesium chloride and carbon dioxide. A study of the reaction showed definitely that the presence of small amounts of triphenylcarbinol in the triphenylchloromethane used to make the reagent very materially lowered the yield of triphenylacetic acid.

The systematic addition of increasing quantities of triphenylcarbinol gave a yield curve shown in Fig. 1 as the lower curve, in which an addition of 15.3 mols per cent. of triphenylcarbinol caused the yield of triphenylacetic acid to drop from 75%[2] to 0%. The upper straight line in Fig. 1 represents the yield of acid to be expected based on the yield of acid without addition of the carbinol and subtracting an amount corresponding to the diminution in yield caused by the reaction of a part of the reagent with the carbinol.

The lowering in yield of acid was not caused by an interference in the reaction of the triphenylchloromethane with the magnesium to form the Grignard reagent, since the same amount of triphenylcarbinol (15.3 mole per cent.) when added after the reagent *had* been prepared prevented the reaction

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[1] Parts of this paper have been presented at the Berkeley and Eugene meetings of the Pacific Division of the American Association for the Advancement of Science and at the Minneapolis meeting of the American Chemical Society.

[2] The maximum yield obtained was 87.5%, but the method used was not adaptable to the study at hand.

with carbon dioxide from taking place. The same result was observed when the mixture was *stirred* and *refluxed* continuously for twenty-four hours. However, in another experiment a similar solution of triphenylmethylmagnesium chloride, containing 15.3 mole per cent. of carbinol was allowed to *stand* in contact with carbon dioxide, at room temperature, for sixty hours. A moderate yield of acid was obtained and is shown in Fig. 1 midway between the two curves mentioned above and is connected with the lower or experimental curve by a dotted line.

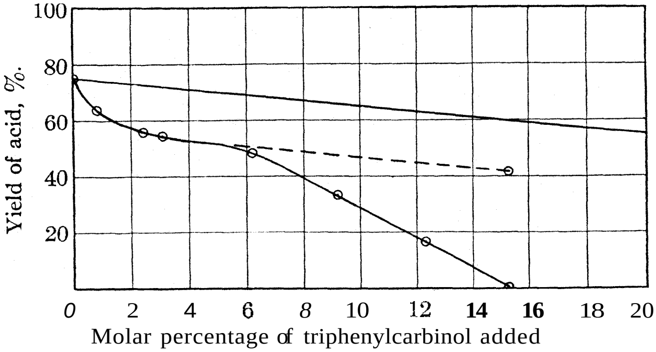


Fig 1—The effect of triphenylcarbinol on the yield of triphenyl acetic acid obtained by the reaction of triphenylmethylmagnesium chloride with carbon dioxide.

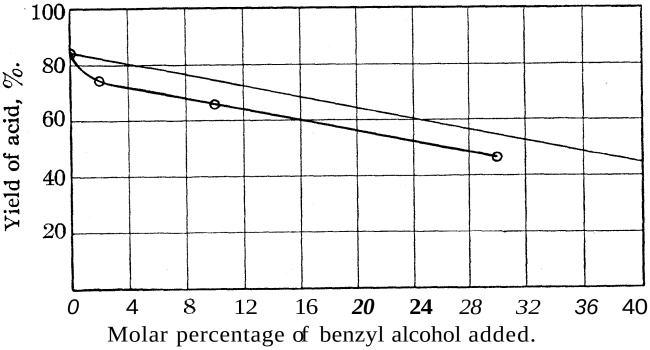


Fig. 2.—The effect of benzyl alcohol on the yield of phenylacetic acid obtained by the reaction of benzylmagnesium chloride with carbon dioxide.

If the curve in Fig. 1 is compared with those of the other reagents investigated (Figs. 2, 3, 4) it will be noted that the curve for triphenylmethylmagnesium chloride differs from all of the others in that there is a downward change in direction of the curve beyond about 6 mole per cent. addition of carbinol, but that the dotted line makes a curve that compares very nicely with all of the others. There seems to be at least two possible explanations of this unique behavior of triphenylmethylmagnesium chloride. In the first place this reagent, as well as many of its reaction products, differs from the other reagents in being much less soluble in ether. The reaction of the reagent with carbon dioxide is accompanied by the solution of the yellowish precipitate of the reagent with the formation of a clear deep blood-red solution which more or less quickly, depending upon the rate of addition of the carbon dioxide, precipitates a yellowish-white substance which is probably the magnesium salt of triphenylacetic acid. When triphenylcarbinol was added, however, in amounts corresponding to the downward drop in the curve (6 mole per cent. or more) the reagent did not dissolve nor was a red solution produced, indicating that in the heterogeneous mixture a new factor influencing the course of the reaction was present. This

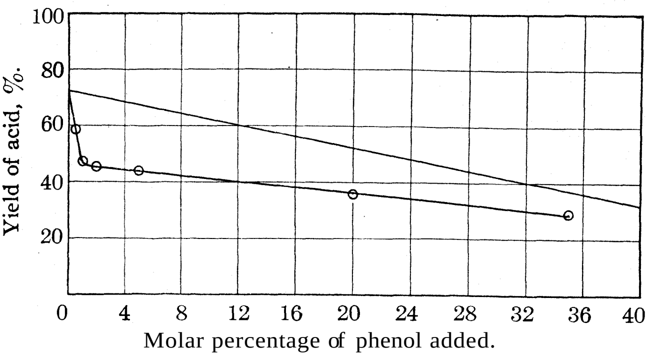


Fig. 3.—The effect of phenol on the yield of benzoic acid obtained by the reaction of phenylmagnesium bromide with carbon dioxide.

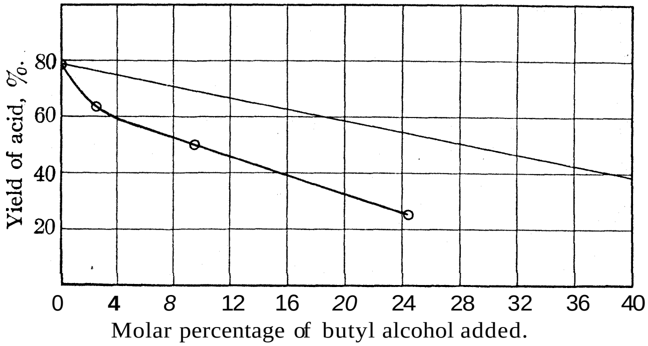
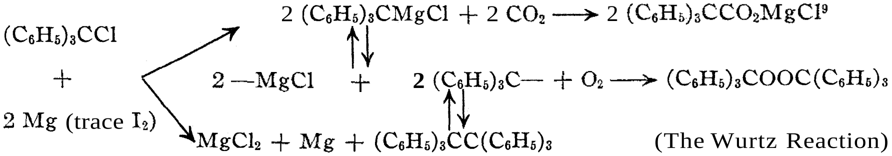


Fig. 4.—The effect of butyl alcohol on the yield of valeric acid obtained by the reaction of butylmagnesium bromide with carbon dioxide.

point on the curve might well correspond to the formation of a precipitate of the magnesium derivative of triphenylcarbinol.

Gilman and McGlumphy[3] and Gomberg and Bachmann[4] have shown recently that triphenylmethylmagnesium iodide may be prepared from triphenylmethyl and magnesious iodide, a reaction which explains the high yields of triarylmethylmagnesium halides from the tertiary halides of the type of triphenylchloromethane. This reaction is incorporated in the combined reactions given below. The reverse process, the dissociation of triphenylmethylmagnesium chloride into triphenylmethyl, seems probable in view of the fact that oxygen[6] reacts smoothly with the solution to give an almost quantitative yield of triphenylmethyl peroxide,[6] a reaction more characteristic of triphenylmethyl than of Grignard reagents.[7] Thus, the reactions of triphenylmethylmagnesium chloride are complicated by the possible presence of triphenylmethyl,[8] which may in part be responsible for the greater effect of triphenylcarbinol on this reagent. These interrelationships are expressed in the following reactions.



$$\begin{tikzcd}
 & 2\,(C_6H_5)_3CMgCl + 2\,CO_2 \arrow[r] \arrow[d, leftrightarrow] & 2\,(C_6H_5)_3CCO_2MgCl^{9} \\
(C_6H_5)_3CCl + 2\,Mg\ (\text{trace } I_2) \arrow[ur] \arrow[dr] & 2\,\text{—}MgCl + 2\,(C_6H_5)_3C\text{—} + O_2 \arrow[r] \arrow[d, leftrightarrow] & (C_6H_5)_3COOC(C_6H_5)_3 \\
 & MgCl_2 + Mg + (C_6H_5)_3CC(C_6H_5)_3 & \text{(The Wurtz Reaction)}
\end{tikzcd}$$

Gilman and St. John[9a] have recently shown that bromomagnesium triphenylcarbinolate when heated in ether solution was transformed slowly into triphenylmethane, and that in the presence of ethylmagnesium bromide the transformation did not take place. This reaction suggests the possibility that triphenylmethane was responsible for the decreased yield of triphenylacetic acid. However, the addition of triphenylmethane to a solution of triphenylmethylmagnesium chloride had little effect on the yield of acid obtained therefrom.

The reagent most closely related to triphenylmethylmagnesium chloride

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[3] Reference 12 of a paper by Gilman and Fothergill, THIS JOURNAL, 51, 3152 (1929).

[4] Gomberg and Bachmann, *ibid.*, 52, **2455** (1930).

[5] Gilman and Fothergill, Ref. 3, p. 3151, have presented other evidence for the dissociation of triphenylmethylmagnesium chloride.

[6] This reaction has been observed by Schmidlin, *Ber.*, **39,** 4183 (1906); 41, 423 (1908).

[7] Several studies of the reaction of Grignard reagents with oxygen have been recorded but peroxides have not been isolated excepting from the triarylmagnesium halides although the assumption has been made by a number of authors that peroxides are formed as intermediates.

[8] Gomberg and Bachmann, Ref. **4,** p. **2456,** have suggested that the presence of triphenylmethyl in the reaction of triphenylchloromethane with magnesium has been the cause of certain misunderstandings in connection with this reagent.

[9] This reaction is affected very greatly by the presence of triphenyl carbinol.

[9a] Gilman and St. John, Rec. *trav. chim.*, November, 1930.

that was studied was diphenylmethylmagnesium chloride. Only small yields of this reagent were obtainable,[10] the major product being tetraphenylethane. The yield, furthermore, was very dependent on the history of the diphenylchloromethane from which the reagent was made, as, for example, a yield of 23% obtained with freshly distilled chloride dropped to 4% by merely allowing the chloride to stand in a brown, glass-stoppered bottle for three weeks.

Many attempts were made by Mr. Langlois in this Laboratory to overcome these difficulties and to dissociate tetraphenylethane in the presence of magnesious iodide, endeavoring to produce diphenylmethylmagnesium chloride in a way similar to the formation of triphenylmethylmagnesium chloride from triphenylmethyl and magnesious iodide and to effect the cleavage of tetraphenylethane with magnesious iodide similar to the cleavage observed with the alkali metals.[11] The reaction, unfortunately, was not realized even working to temperatures as high as 300° in an atmosphere of carbon dioxide.

The effect of diphenylcarbinol on the reaction of diphenylmethylmagnesium chloride with carbon dioxide could not be determined accurately because of the experimental difficulties with the reagent. One comparable result is given in the experimental part which shows only a slight diminution of the yield. This small effect may be masked by the presence of diphenylcarbinol in the chloride used to make the reagent.

The results obtained for phenylmethyl or benzylmagnesium chloride, phenylmagnesium chloride and butylmagnesium bromide were more conclusive (Curves 2, 3, 4). In the reaction of all of these reagents with carbon dioxide the presence of a small quantity of the alcohol or phenol corresponding to the reagent produced a marked drop in the yield of acid beyond that caused by the expected reaction of the carbinol with a part of the reagent. The latter is shown by the upper line in each diagram. Further additions caused further diminutions in the yields of the acids, but the lowering of the yield was much less precipitous.

The results shown in the diagrams (1, 2, 3, 4) above were all obtained by adding the carbinol along with the organo halide from which the reagents were made. The effects of adding the carbinol after the reagents had been made are shown in Table I, in which it is to be noted that in all cases, except the action of phenol on phenylmagnesium bromide, about the same lowering in yield was obtained. With the exception mentioned the loss in yield was considerable while not nearly as great as that caused by adding the phenol with the phenyl bromide when making the reagent.

The effect of adding phenol to triphenylmethylmagnesium chloride and

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[10] Gilman and Zoellner, THIS JOURNAL, 52, 3984 (1930), have succeeded recently in materially increasing the yield of this reagent and the acid obtained from it.

[11] Ziegler and Thielmann, Ber., 56B, 1740 (1923).

TABLE I

RESULTS OR EXPERIMENTS

Reagent	Mole per cent of carbinol added	Yield to be expected, %	Yield adding carbinol	
			before, %	after, %
Triphenylmethylmagnesium chloride	15.3	59 7	0	0
Benzylmagnesium chloride	10	74.5	65 8	62.5
Phenylmagnesium bromide	1	71 1	47	61 4
Butylmagnesium bromide	9.5	68 9	50	48

triphenylcarbinol to phenylmagnesium bromide was determined in attempting to find some explanation for the catalysis. In these two determinations the yields of the acids were about the expected amount based on the maximum yields and subtracting for the amount of carbinol added. Thus the effect appears to be concerned with the carbinol corresponding to the Grignard reagent. However, the reaction of triphenylmethylmagnesium chloride with carbon dioxide was very materially affected by the addition of small quantities of benzaldehyde, the addition of 28.4 mole per cent. of benzaldehyde being sufficient entirely to prevent the formation of the acid with carbon dioxide. These results are shown in Fig. 5, the depression curve being the lower straight line.

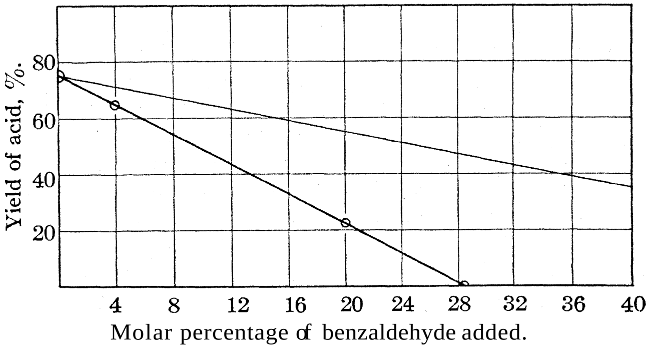

Fig. 5.—The effect of benzaldehyde on the yield of triphenylacetic acid obtained by the reaction of triphenylmethylmagnesium chloride with carbon dioxide.

The explanation offered for the depressing effect of benzaldehyde is that the reagent reacted with the aldehyde, forming the magnesium derivative of α,β,β,β-tetraphenylethyl alcohol, which appears to be about half as effective as triphenylcarbinol.

The addition of alcohols to the reaction of Grignard reagents with carbonyl compounds other than carbon dioxide would be expected to cause very little lowering of the yield because of the fact that high yields are obtainable from the reaction in spite of the fact that magnesium alcoholates are produced as the reaction progresses.

$$RMgX + RCHO \longrightarrow R_2CHOMgX$$

This view was tested in one experiment only in which 2.43 mole per cent. of butyl alcohol was added to butylmagnesium bromide and then the reagent allowed to react in the usual way with benzaldehyde. The lowering in yield was 2.5% as compared with the addition of 2.43%.

The mechanism of the catalytic effect of the presence of magnesium alcoholates on the reaction of Grignard reagents with carbon dioxide is not clear at this time. The curves seem to have a characteristic shape and the percentage depression is much greater for smaller additions of the alcohol. Some further studies under way may help to clear this up.

Experimental Part

Reactions Involving Triphenylmethylmagnesium Chloride.—The triphenylmethylmagnesium chloride was prepared in essentially the way that Gilman and Zoellner[12] recommend, except that we did not carry out the reaction under an inert atmosphere. This probably is quite advantageous as we obtained an increase of 12.5% in the yield of triphenylacetic acid by carrying out the entire reaction in an astmosphere of dry carbon dioxide (compare Expt. 4 with 3).

Especial care was taken to free the triphenylchloromethane from impurities by dissolving the crude product of the Friedel and Crafts reaction in a minimum of boiling chloroform followed by dilution with three volumes of ether as the solution cooled. The chloride crystallized well, the recovery was good and the color was practically removed. The material was then recrystallized from boiling gasoline as it was found that the trace of chloroform present interfered with the reaction. The melting point was 115°. Moisture should be excluded from the chloride as the hydrogen chloride produced as well as the carbinol was found to be an active negative catalyst.

Crude triphenylchloromethane direct from the Friedel and Crafts synthesis was quite reactive. Several preparations were found to react smoothly with magnesium to form the Grignard reagent, while the more purified material described above did not. This led to an investigation of the effect of anhydrous aluminum chloride, which may have been present in the crude material, as a catalyst for the Grignard reaction. Anhydrous aluminum chloride did start the reaction nicely, but the yield of triphenylacetic acid was somewhat lower than when using iodine. For the preparation of triphenylacetic acid, freshly prepared crude chloride from the Friedel and Crafts reaction gives yields sufficiently high to make the purification of the halide unprofitable.

Since we were studying the effect of adding various substances to the reaction it was not convenient to carry out the reaction in an atmosphere of carbon dioxide. The procedure used was briefly as follows: 7 g. of the purified triphenylchloromethane, 0.2 g. of iodine, 2 g. of powdered magnesium and 200 cc. of sodium-dried ether were allowed to react for one hour with stirring and gentle refluxing. Carbon dioxide was then admitted and the stirring and refluxing were continued for three hours. The mixture was then decomposed and the triphenylacetic acid isolated according to Schmidlin.[13] In Table II are given the results of a number of experiments which have some variation from this general procedure and which show the effect of the history of the chloride used, the substitution of aluminum chloride for the iodine, etc.

The addition of triphenylcarbinol lowered the yield of triphenylacetic acid according to the results listed in Table III. The carbinol added is given in mole per cent. of the chloride used in making the reagent. The

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[12] Gilman and Zoellner, THIS JOURNAL, 51, 3493 (1929).

[13] Schmidlin, *Ber.*, 39, 634 (1906).

TABLE II

RESULTS OF EXPERIMENTS

No.	Variation in the experiment	Yield of triphenylacetic acid, %
1	Chloride recryst. from CH_3COCl	66 and 41.5
2	Chloride recryst. from $CHCl_3$–Et_2O	16.6
3	Chloride recryst. from $CHCl_3$–Et_2O, then gasoline	75 and 75
4	Same as No. 3 except CO_2 was passed in before introducing the chloride	87.5 (86.4 with 0.2 g. of triphenylmethyil peroxide in addition)
5	Same as No. 4 except that freshly made crude chloride from the Friedel and Crafts reaction was used	81.6 and 81.6
6	Used 0.1 g. of $AlCl_3$ (anhyd.) instead of iodine to start the reaction	60.8 (67.8 with 0.2 g. of I_2 in addition)
7	Passed in dry HCl for 30 sec., no iodine	0 (29 with 0.2 g. of I_2 in addition)

carbinol was added with the chloride and then the experiment was treated exactly as Expt. 3, Table II.

TABLE III

RESULTS OF EXPERIMENTS

	1	2	3	4	5	6	7	8
Mole per cent. of $(C_6H_5)_3COH$ added before the preparation of the Grignard reagent	0	0.8	2.4	3.1	6.2	9.2	12.3	15.3
Yield of triphenylacetic acid, %	75	63.5	58.0	52.5				
			55.3	55.3	48.4	33 2	16.6	0
	75			56.0	.			

In Table IV 15.3 mole per cent. of triphenylcarbinol was added in each case after the chloride had reacted for one hour and the Grignard reagent had formed normally, but before the carbon dioxide was passed through the flask.

TABLE IV

RESULTS OF EXPERIMENTS

No.		Yield, %
1	15.3 mole per cent. of carbinol added after the reagent had been formed	0
2	Same as No. 1, except that the mixture was allowed to stand with carbon dioxide for about 60 hours	41.5
3	Same as No. 1 except the mixture was refluxed and stirred for 24 hours	0

The yield of acid when 50% of phenol was added was 31.9%.

In order to determine whether the chloromagnesium triphenylcarbinolate was responsible for the decreased yield of triphenylacetic acid (by causing the latter substance to decompose during the reaction), 1 g. of triphenylcarbinol and 6.86 g. of triphenylacetic acid were added to ethylmagnesium bromide made from 0.05 mole of ethyl bromide. The mixture was refluxed in ether for seven hours and the triphenylacetic acid recovered in the usual way. The weight of acid was 6.55 g., showing that very little decomposition took place.

Reactions Involving Diphenylmethylmagnesium Chloride and Tetraphenyl Ethane.[14]—The preparation of diphenylmethylmagnesium chloride was quite similar to that given by Gilman and Kirby.[15] The best yield of diphenylacetic acid was obtained from freshly distilled chloride and amounted to 23.8% in a 0.05-mole experiment. The remainder of the material was recovered practically quantitatively as tetraphenylethane (6 4 g.). The chloride was redistilled and a yield of 9.0% was obtained when 1 g. of diphenylcarbinol (0.0054 mole) was added to the same quantity of reagent.

The dissociation of tetraphenylethane in the presence of magnesious iodide was attempted in an atmosphere of carbon dioxide in a boiling ether–benzene mixture, in boiling xylene, in a kerosene fraction at 200°, and in a mixture of isoamyl ether and anthracene at 300°, but in no case was any diphenylacetic acid isolated. The tetraphenylethane was recovered unchanged.

Reactions Involving Benzylmagnesium Chloride.—The method of preparation of benzylmagnesium chloride was that of Gilman and McCracken.[16] The benzyl chloride of a C. P. grade was shaken with cold concentrated sulfuric acid to remove any benzyl alcohol or other easily sulfonated substances, neutralized with anhydrous potassium carbonate, filtered and fractionated. The fraction used boiled constantly at 91° under diminished pressure. An excess of magnesium clippings and 0.2 g. of iodine were used with 0.1 mole of benzvl chloride in all of the reactions. The chloride was allowed to react with the magnesium for one hour and the carbon dioxide was passed over the surface of the liquid for three hours. The temperature control was found to be very important. The best procedure was to cool the reaction mixture to 10° as the benzyl chloride was added over a period of forty-five minutes, followed by a fifteen-minute refluxing, then cooling again to 10° while the carbon dioxide was passed into the flask.

TABLE V

EXPERIMENTAL RESULTS

Amount of benzyl alcohol added, mole per cent.	0	2	10	30
Yield of phenylacetic acid, %	84.5	74.3	65.8	46.3

The yield of phenylacetic acid obtained upon adding 10% of benzyl alcohol after the preparation of the reagent was 62.5%.

Reactions Involving Phenylmagnesium Bromide.—The method of preparing the phenylmagnesium bromide was that given by Gilman and Parker.[17] The bromobenzene was a C. P. grade and was fractionated twice through an efficient column filled with Lessing contact rings. The fraction used boiled at 146° at 640 mm. pressure. One-tenth mole experiments were made with an excess of magnesium clippings and 0.2 g. of iodine. The yield of benzoic acid was determined by extracting the alkali-soluble material with potassium hydroxide solution. followed by acidification, and repeated ether extraction. The ether solution was evaporated and the yield of benzoic acid determined

TABLE VI

EXPERIMENTAL RESULTS

	1	2	3	4	5	6	7
Mole per cent. of phenol added	0	0.5	1	2	5	20	35
Yield of benzoic acid, %	72.1	58.6	46.8 47.2	45.1	43.7	35.9	29.1

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[14] Experimental work done by David P. Langlois.

[15] Gilman and Kirby, THIS JOURNAL, 48,1735 (1926).

[16] Gilman and McCracken, *ibid.*, 45, 2462 (1923).

[17] Gilman and Parker, ibid., 46, 2816 (1924).

by subtracting the weight of phenol added to the reaction from the crude weight of benzoic acid.

The yield of benzoic acid obtained by adding 1% of phenol after the reagent had been prepared was 61.4 and 63.5% when 15.3 mole per cent. of triphenylcarbinol was added in the same way, In the latter experiment 40% of the triphenylcarbinol was recovered as triphenylmethyl peroxide.[18]

Reactions Involving Butylmagnesium Bromide.—The preparation was essentially that of Gilman and Parker.[17] The butyl bromide was a C. P. grade and was further purified by shaking with cold concentrated sulfuric acid and by fractionation through a column filled with Lessing contact rings. The bromide boiled at 94.5° at 640 mm. pressure. An excess of magnesium clippings and 0.2 g. of iodine were used with 0.1 mole of butyl bromide in each experiment. The yield was determined by extracting the acid with alkali, liberating the acid with hydrochloric acid, collecting the product with ether and finally fractionating the ether–valeric acid mixture.

TABLE VII

EXPERIMENTAL RESULTS

	1	2	3	4
Mole per cent. of butyl alcohol added	0	2.43	9.46	24.3
Yield of valeric acid, %	78.4	63.5	60.0	26.2

The yield of valeric acid obtained by adding 9.5% of butyl alcohol after the reagent had been prepared was 48.0%.

The normal reaction of butylmagnesium bromide with benzaldehyde gave a yield of 62.2% of phenylbutylcarbinol. Upon adding 2.43 mole per cent. of butyl alcohol after the reagent had been prepared, but before the addition of the benzaldehyde, the yield was lowered to 59.7%, a loss of 2.5%.

Summary

Curves are given showing the depression in yield of the reaction of several Grignard reagents with carbon dioxide caused by the addition of relatively small quantities of the alcohols corresponding to the reagents. Reactions are given which indicate an equilibrium relationship between triphenylmethylmagnesium chloride and triphenylmethyl. Cleavage of tetraphenylethane with magnesious iodide was not successful.

SALT LAKE CITY, UTAH

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[18] The explanation of this result may he found in Gomherg and Rachmann's paper, Ref. 4.

[CONTRIBUTION PROM THE CHEMICAL LABORATORY OR THE UNIVERSITY OF ARKANSAS]

DERIVATIVES OF DULCIN[1]

BY E. WERTHEIM

RECEIVED AUGUST 30, 1930 PUBLISHED JANUARY 12, 1931

Since the first preparation of dulcin many derivatives of this interesting compound have been made. In some of these the character of the N side chain has been altered[2] while in others there is a duplication of function[3] or a substitution of various groups on the benzene ring.[4] Certain generalizations have been drawn relative to the effect of constitution upon taste[5] but the state of existing knowledge of this subject is unsatisfactory because an insufficient number of derivatives has been examined. The preparation of new derivatives as reported in this and other papers was undertaken in this Laboratory in the hope of obtaining a more complete understanding of the basic problem.

Reaction of Dulcin with Ethyl Chloroformate.—This reaction yields both types of derivatives noted above, those with altered side chain and with duplicated function. The following compounds were prepared: ethyl p-phenetyl-allophanate, *p*-phenetyl-biuret, bis-(*p*-phenetyl)-urea and bis-(*p*-phenetyl)-biuret. All were found to be tasteless.

Sulfur Derivatives of Dulcin.—*p*-Anisyl- and *p*-phenetyl-thiourea have already been prepared.[6] The taste of the former has not been reported; the latter is very bitter.[7] A bitter taste is characteristic for the reported aromatic thioureas while numerous urea compounds are sweet tasting. In the thioanisyl- and thiophenetyl-urea reported herein (isomeric with the compounds of Dyson and George) the thio-ether group (normally giving a bitter taste) is "opposed" to the carbamido group. The result in each case is a practically tasteless compound. Thioanisyl- and thiophenetyl-thiourea in which both oxygen atoms are substituted by sulfur were also prepared. These derivatives have a strongly bitter taste which is very lasting.[8]

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[1] Paper No. 215, Journal Series, University of Arkansas.

[2] Lumière and Perrin, *Bull. soc. chim.*, [3] *29,* 966 (1903); Borsche, *Ann.*, **334**, 185 (1904); Lange, Ebert and Youse, THIS JOURNAL, **51**, 1912 (1929); Gilman and Hewlett, *Iowa State College J. Sci.*, **4**, No. 1, 27–33 (1929).

[3] Interesting examples of such duplication are found in the diureido derivatives of phenetole (*cf.* Lorang's paper).

[4] Spiegel, Munblit and Kaufmann, *Ber.*, 39,3243 (1906); Lorang, *Rec. trav. chim.*, 47, 179 (1928) (contains a review of previous work).

[5] Thate, *ibid.*, 48, 116 (1929); *cf.* also Lorang's paper.

[6] Dyson and George, *J. Chem. Soc.*, *125,* 1708 (1924).

[7] Cohn, "Die Organischen Geschmacksstoffe," F. Siemenroth, Berlin, **1914**, p. **747.**

[8] The compounds were tasted by the writer and three advanced students who passed a preliminary training and examination using solutions of dulcin and saccharin. All compounds and solutions were given code numbers and no discussion of results was per-

Experimental Part

Ethyl *p*-**Phenetyl-allophanate.** *p*-$EtOC_6H_4NHCONHCO_2Et$.—A mixture of 20 g. of dulcin and 10 g. of ethyl chloroformate was heated in the free flame until homogeneous and then in an oil-bath maintained at a temperature of 100° for two hours. Upon cooling the mix solidified. It was twice recrystallized from hot amyl alcohol or from equal parts of amyl and ethyl alcohols. The crystals were washed with petroleum ether and ethanol; yield, about 3.5 g.; white needles, m. p., 139–140°; tasteless; soluble in benzene, xylene, ethanol, amyl alcohol, hot water and acetic acid.

p-Phenetyl-biuret, *p*-$EtOC_6H_4NHCONHCONH_2$.—Four grams of ethyl *p*-phenetyl-allophanate together with 10 cc. of concentrated ammonium hydroxide was placed in a sealed tube and heated to a temperature of 100" for four hours. At this time the tube contained a white solid and red supernatant liquid. The materials were washed from the tube with hot water and, after neutralization with dilute hydrochloric acid, subjected to filtration. The solid was dried, after which it was well washed with hot benzene (to remove unchanged allophanate), followed by petroleum ether. After recrystallization from dilute acetic acid the compound had a melting point of 185–186°; yield, 1.3 g.; white, amorphous, tasteless compound; soluble in ethanol, hot xylene, acetic acid; sparingly soluble in benzene.

Bis-(*p*-phenetyl)-urea, (*p*-$EtOC_6H_4NH)_2CO$.—A mixture of 5 g. of ethyl chloroformate and 18 g. of dulcin was heated in an oil-bath for two hours at a temperature of 175". The resulting solid was washed with hot ethanol and filtered by suction. It was next washed several times with hot acetic acid, then with ether. (The acetic acid solution was reserved—see below.) The compound was recrystallized from benzyl alcohol and washed with ether: yield, 0.6 g.; white microscopic needles; tasteless; melting point, 225–226°. The identity of the compound was confirmed by analysis for nitrogen.[9]

Bis-(*p*-phenetyl)-biuret, (*p*-$EtOC_6H_4NHCO)_2NH$.—The acetic acid washings of diphenetyl-urea (see above) when chilled in ice water gave a precipitate which was removed by filtration and washed with ether; yield, 1.4 g.; m. p., 208–209°; white microscopic oblong platelets; tasteless.

TABLE I

ANALYTICAL DATA OF DULCIN DERIVATIVES

Compound	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ethyl *p*-phenetyl allophanate	$C_{12}H_{16}O_4N_2$	57.15	56.71 57.11	6.35	6.98 6.50	11.11	11.01
p-Phenetyl-biuret	$C_{10}H_{13}O_3N_3$	53.81	53.48 53.71	5.83	7.40 5.85	18.83	18.51
Bis-(*p*-phenetyl)-biuret	$C_{18}H_{21}O_4N_3$	62.99	62.99	6.12	6.31	12.24	11.96 11.97

p-**Nitrothiophenol.**—This compound was prepared essentially as directed by Mayer.[10] The yield from 31 g. of nitrochlorobenzene was about 10 g.

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mitted. In all cases the solid compounds were tasted, also the following solutions, (1) 0.01 g. of compound in 500 cc. of water (38°), (2) 0.01 g. of compound in 50 cc. of ethanol made up to 500 cc. with water. The limited solubility of the compounds prevented the preparation of more concentrated solutions.

[9] This compound was previously reported by Gattermann and Cantzler, *Ber.*, 25, 1090 (1892), m. p. 225–226°; by Sonn, *ibid.*, 47, 2441 (1914), m. p. 225" and by Migliacci and Gargiulo, *Gazz. chim. ital.*, 58, 110 (1928), m. p. 220°.

[10] Mayer, *Ber.*, 42, 3050 (1909).

p-**Nitrothiophenetole.**—This was made from **20** g. of p-nitrothiophenol, **3** g. of sodium, **20** g. of ethyl iodide and about **100** cc. of ethanol as outlined by Monier-Williams;[11] yield, 15–20 g.

p-**Nitrothioanisole.**—The same method was used as for nitrothiophenetole. From **20** g. of p-nitrothiophenol, **3** g. of sodium. **24** g. of methyl iodide and about **100** cc. of methyl alcohol a yield of about **15** g. was realized.[12]

p-**Thiophenetidine.**—The directions of Monier-Williams were followed:'' **20** g. of p-nitrothiophenetole, **39** g. of tin and **62** cc. of concentrated hydrochloric acid gave a yield of about **12** g.

p-**Thioanisidine.**—*p*-Nitrothioanisole was reduced with zinc dust and hydrochloric acid. The directions of Zincke and Jörg[13] were modified in that the preparation was set aside for only three hours and that solid sodium sulfate was used to precipitate the amine sulfate. Twenty grams of nitrothioanisole gave **8–10** g. of the final product.

p-**Thiophenetylurea,** p-$\mathrm{EtSC_6H_4NHCONH_2}$.—Five grams of *p*-thiophenetidine was put into solution in **50** cc. of water upon the addition of **5** cc. of concentrated hydrochloric acid. **A** solution of **5** g. of potassium cyanate in **25** cc. of water was added in small amounts whiie the flask was given a thorough shaking. The resulting precipitate was dried and subsequently recrystallized from acetone: yield, **2.5** g.; m. p. 149–150°; glistening white platelets; soluble in the common organic solvents and in hot water. With concentrated sulfuric acid a colorless solution is formed which becomes pale green upon application of heat and again colorless. The solid compound produces a stinging effect upon the tip of the tongue followed by a very slight bitter taste. The prepared solutions were tasteless.

p-**Thioanisylurea,** p-$\mathrm{MeC_6H_4NHCONH_2}$.—Four grams of *p*-thioanisidine dissolved in *a* solution of **2.35** cc. of concentrated hydrochloric acid and **40** cc. of water was treated with **1.8** g. of potassium cyanate in **25** cc. of water. The compound was recrystallized when dry from dilute ethanol plus a few drops of ammonium hydroxide; yield, **1** g.; white needles, m. p. **164–165'**; tasteless.

p-**Thiophenetylthiourea,** p-$\mathrm{EtSC_6H_4NHCSNH_2}$.—Solutions of 2 g. of *p*-thiophenetidine in **15** cc. of water and **2** cc. of concentrated hydrochloric acid, and **2** g. of ammonium thiocyanate in **10** cc. of water were mixed and slowly evaporated to dryness. The dry mass was allowed to stand for about twenty hours, then pulverized and washed with water. It was next covered with hot ethanol, which was subsequently removed by filtration. When cooled the ethanol solution deposited the compound in light yellow platelets: yield, **0.5** g.; m. p. 136–137°; lasting bitter taste.

p-**Thioanisylthiourea,** p-$\mathrm{MeC_6H_4NHCSNH_2}$.—Five and four-tenths grams of *p*-thioanisidine was treated with **25** cc. of water and **3.12** cc. of concentrated hydrochloric acid. The solution was filtered and mixed with a solution of **2.65** g. of ammonium

TABLE II

SULFUR DERIVATIVES OF DULCIN

Compound	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur. % Calcd.	Sulfur. % Found
p-Thiophenetylurea	$C_8H_{12}ON_2S$	55.09	55.21	6.12	6.32	14.29	14.44 14 34	16.32	16.25
p-Thioanisylurea	$C_8H_{10}ON_2S$	52.75	52.99	5.49	5.43	15 38	15 47 15 32	17 58	17.46
p-Thiophenetylthiourea	$C_9H_{12}N_2S_2$	50.95	50.75	5.66	5.76	13.21	13 18	30 19	29 87
p-Thioanisylthiourea	$C_8H_{10}N_2S_2$	48.49	48.72	5.05	4.94	14.14	14.28	32 32	31.89 31 78

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[11] Monier-Williams, J. *Chem. Soc.*, *89*, 278 (1906).

[12] Blanksma, *Rec. trav. chim.*, *20*, *403* (1901).

[13] Zincke and Jorg, *Ber.*, 44,620 (1911).

thiocyanate in 25 cc. of water. The combined solution was slowly evaporated until a friable solid mass was obtained. This was allowed to stand overnight, then pulverized and washed with boiling water. It was then repeatedly washed with hot water, made strongly ammoniacal and alkaline by the use of sodium and ammonium hydroxide solutions. The compound was finally washed with ethanol and with ether. Some was recrystallized from benzyl alcohol but was not improved by this treatment: yield, about 4 g.; platelets of faint yellow color, m.p. 198–199°; persistent bitter taste.

Summary

Derivatives of dulcin have been prepared in which the N side chain is altered and in which the phenetyl group is duplicated; these are tasteless. Substitution of the ether oxygen of dulcin by sulfur gives tasteless derivatives, while substitution of both oxygens by sulfur yields compounds with a very bitter taste. Seven new compounds are reported.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. VI. THE PYROLYSIS OF NATURAL RUBBER IN THE PRESENCE OF METALLIC OXIDES

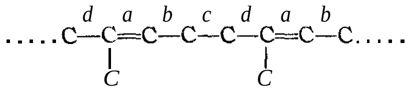
BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED SEPTEMBER 2, 1930 PUBLISHED JANUARY 12, 1931

The first paper of this series[1] describes the influence of metals on the pyrolysis of natural rubber: it shows that the presence of a metal does not change the nature of the pyrolysis products, but affects their relative proportions. In this respect magnesium and zinc are most active. The fact that both zinc oxide and magnesium oxide influence the vulcanization process makes it desirable to study the influence of these compounds on the pyrolysis of rubber.

Experiments similar to these previously reported show that zinc oxide or magnesium oxide acts similarly to zinc or magnesium; zinc oxide has by far the stronger effect. Briefly the nature and proportion of pyrolysis products obtained with zinc oxide duplicate those obtained with magnesium, within experimental error.

Let the rubber molecule be represented by a long open-chain formula, and the various bonds of the chain be designated by letters



$$\cdots\cdots\mathrm{C}\overset{d}{-}\underset{\overset{|}{C}}{\mathrm{C}}\overset{a}{=}\mathrm{C}\overset{b}{-}\mathrm{C}\overset{c}{-}\mathrm{C}\overset{d}{-}\underset{\overset{|}{C}}{\mathrm{C}}\overset{a}{=}\mathrm{C}\overset{b}{-}\mathrm{C}\cdots\cdots$$

The relative numbers of ruptures at a, b, c and d during the pyrolysis of straight rubber have been computed from the data previously reported, and are represented by $a = 0$, $b = 0.6$, $c = 100$ and $d = 0.7$. However, a similar computation indicates that, in the case of rubber pyrolyzed with

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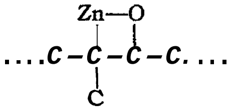
[1] Midgley and Henne, THIS JOURNAL, 51, 1215 (1929).

magnesium, the ruptures are as follows: $a = 0$, $b = 12.7$, $c = 100$ and $d = 12.1$. In both cases b equals d within experimental error.

Since zinc oxide has the same effect as magnesium upon pyrolysis, it appears that its presence multiplies by about 17 the number of ruptures of the b and d-bonds.

If d and b derive their strength from the fact that they are adjacent to the double bond a, it may be expected that any agent affecting the unsaturation of *a* will increase the similarity of d and b to c. If the agent be such as to remove entirely the unsaturated character of a, the bonds d, b and c might even become almost identical in strength, though complete identity would be prevented by the presence of the methyl side chains.

However, the formation of a chemical individual such as



$$\begin{array}{ccccccc} & & \mathrm{Zn} & - & \mathrm{O} & & \\ & & | & & | & & \\ \ldots\mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C}\ldots \\ & & | & & & & \\ & & \mathrm{C} & & & & \end{array}$$

with a zinc oxide molecule linked on the carbon chain by chemical valences does not seem to be supported by the facts: the pyrolysis products do not contain any compound formed by rupture of the chain at a; no oxygenated product is to be detected; and zinc oxide is not in the least reduced to the metal. Moreover, the seventh paper of this series shows that ruptures of *a* do occur in the pyrolysis of hard rubber where a is chemically saturated with sulfur.

Summary

Pale crepe rubber pyrolyzed in the presence of zinc oxide or magnesium oxide gives the same decomposition products as in the absence of the oxides, but in different proportions. This modification is attributed to an action of the oxides upon the double bonds of the rubber molecule.

COLUMBUS, OHIO

[Contribution from the Chemical Laboratory of Harvard University]

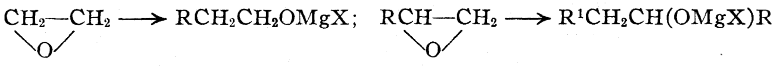
THE ACTION OF ORGANIC MAGNESIUM COMPOUNDS ON ALPHA OXIDO KETONES AND ESTERS

By E. P. Kohler, N. K. Richtmyer and W. F. Hester

Received September 8, 1930 Published January 12, 1931

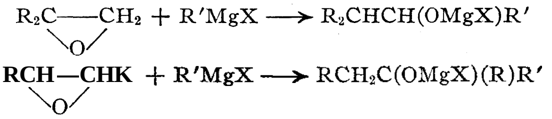
Oxido ketones and glycidic esters have two unsaturated groups in a relation which in other unsaturated compounds is known as conjugated. This relation, doubtless, is responsible for the ease with which they can be rearranged, but, owing to the nature of the reagents employed hitherto, little is known about the intermediates in these rearrangements. We have therefore undertaken an investigation of the behavior of representative oxido ketones and esters toward organic magnesium compounds, since these are capable of forming stable addition products with ethylene oxides as well as with ketones and esters.

From the work of Grignard[1] and a number of later investigators[2] it is known that organic magnesium compounds react much less readily with ethylene oxides than with ketones and esters. It is known also that the outcome of a reaction between an organic magnesium compound and an oxide depends almost entirely upon the number of hydrocarbon residues bounding the oxide ring. Thus the products which are obtained from ethylene oxide itself, and from its mono-alkyl and mono-aryl derivatives, indicate that the reagent opens the ring in the manner to be expected from other reactions of these oxides



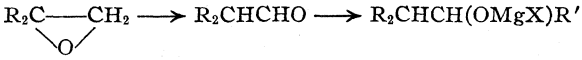
$$\underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow RCH_2CH_2OMgX; \quad \underset{\diagdown O \diagup}{RCH{-}CH_2} \longrightarrow R^1CH_2CH(OMgX)R$$

But no such simple reaction occurs in the case of disubstituted oxides



$$\underset{\diagdown O \diagup}{R_2C{-}CH_2} + R'MgX \longrightarrow R_2CHCH(OMgX)R'$$
$$\underset{\diagdown O \diagup}{RCH{-}CHK} + R'MgX \longrightarrow RCH_2C(OMgX)(R)R'$$

In order to account for these "abnormal" products it is customary to assume that the Grignard reagent first rearranges oxides of this type to the corresponding aldehydes or ketones and then combines with these rearrangement products in the usual manner



$$\underset{\diagdown O \diagup}{R_2C{-}CH_2} \longrightarrow R_2CHCHO \longrightarrow R_2CHCH(OMgX)R'$$

In agreement with what would be expected from an application of these facts to an oxido ketone in which the carbonyl group is not attached to

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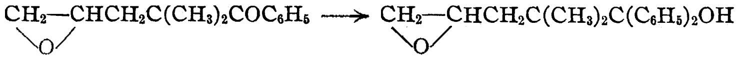
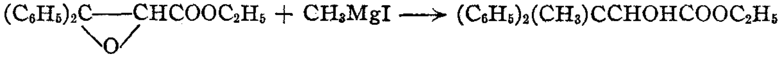
[1] Grignard, *Compt. rend.*, 136, 1260 (1903).

[2] See for example Fourneau and Tiffeneau, Bull. *soc. chim.*, [4]33, 741 (1905); *Compt. rend.*, 145, 439 (1907); Hess, Ber., 46, 3117 (1913); Henry, *Compt. rend.*, 145, 21, 406, 453 (1907).

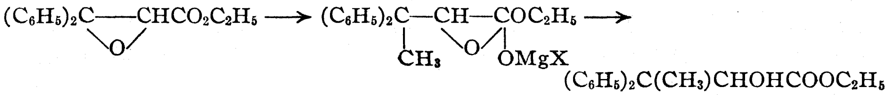
the oxide ring, Haller and Ramart-Lucas[3] found that in a substance of this type the carbonyl group alone was attacked, despite the fact that a highly branched chain must have created a considerable hindrance to the reaction

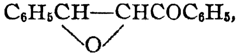


More interesting was a result reported by Bardon and Ramart[4] in the only case in which an organic magnesium compound has been allowed to react with a substance in which an oxido and a carbonyl group are adjoining



Here the carbonyl group reappeared intact, the ring was opened in a unique manner, and, since the authors obtained the same substance in boiling ether as in a freezing mixture, the primary product had to be a magnesium derivative of such a character as to prevent further reaction. A result like this could be explained only by 1,4-addition to the conjugated system

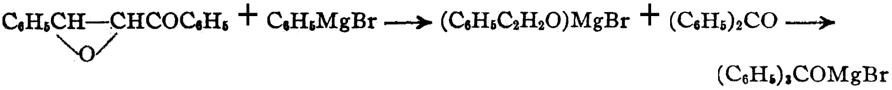


Our own experiments began with the oxide of benzal acetophenone,  a solid α-oxido ketone which can be obtained in a perfectly pure state and in any desired quantity. In view of the results reported by Bardon and Ramart, the behavior of this substance was surprising. It reacted very readily with two molecules of phenyl magnesium bromide and gave one molecule of triphenyl carbinol. It also reacted in a similar manner with ethyl magnesium bromide and gave phenyl diethyl carbinol. The reaction therefore results in cleavage, the hydrocarbon residues from the two molecules of the magnesium compound appear in the carbinol, and the cleavage is not due to an accumulation of phenyl groups.

In addition to the carbinol, the reaction between the oxido ketone and magnesium compounds yielded only resins, which are evidently due to extensive polymerization. Since these resins were of no service it became necessary to resort to a less symmetrical oxido ketone in order to establish the point of cleavage. To this end the oxide of anisal acetophenone was prepared and added to excess of phenyl magnesium bromide in the same manner. It likewise gave triphenyl carbinol and a resin. It was evident, therefore, that the cleavage occurred between the carbinol group and the oxido ring, and it seemed likely that it took place during the early stages of the reaction

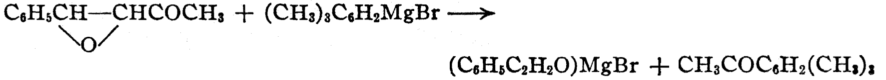
[3] Haller and Ramart-Lucas, Compt. rend., 159, 146 (1914).

[4] Bardon and Ramart, *ibid.*, 183,214 (1926).



$$C_6H_5\underbrace{CH\text{—}CH}_{O}COC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5C_2H_2O)MgBr + (C_6H_5)_2CO \longrightarrow (C_6H_5)_3COMgBr$$

That one of the primary cleavage products is a ketone was definitely established by treating the oxide of benzal acetone with mesityl magnesium bromide, this combination having been selected became if any aceto mesitylene were formed it would survive, since organic magnesium compounds do not combine with mesitylenic ketones. In addition to the usual resin, this combination gave only aceto mesitylene



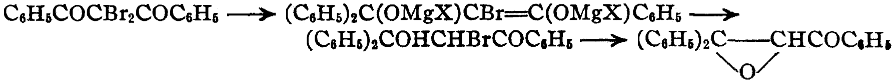
$$C_6H_5\underbrace{CH\text{—}CH}_{O}COCH_3 + (CH_3)_3C_6H_2MgBr \longrightarrow (C_6H_5C_2H_2O)MgBr + CH_3COC_6H_2(CH_3)_3$$

Having established both the stage and the place of this peculiar cleavage, it now became necessary to secure information on the second cleavage product. It seemed improbable that this could be accomplished without employing more highly substituted oxido ketones which might give magnesium derivatives less prone to polymerization. No such substances were known and none could be made by known methods of preparation. After many vain attempts we finally secured one in the following manner.

It has long been known that phenyl magnesium bromide removes bromine from a-bromo ketones and forms magnesium derivatives of the corresponding enols[5]

$$RCHBrCOC_6H_5 + 2C_6H_5MgBr \longrightarrow RCH{=}C(OMgBr)C_6H_5 + C_6H_5C_6H_5 + MgBr_2$$

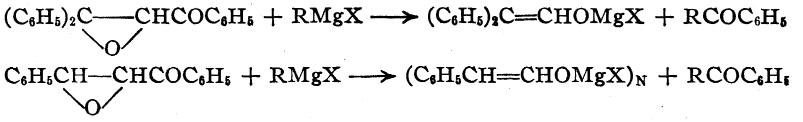
Applied to dibromo dibenzoyl methane, this process resulted in a bromohydrin that was readily converted into an a-oxido ketone of known structure



$$C_6H_5COCBr_2COC_6H_5 \longrightarrow (C_6H_5)_2C(OMgX)CBr{=}C(OMgX)C_6H_5 \longrightarrow \underset{\text{I}}{(C_6H_5)_2COHCHBrCOC_6H_5} \longrightarrow \underset{\text{II}}{(C_6H_5)_2\underbrace{C\text{——}CH}_{O}COC_6H_5}$$

I II

When this new oxido ketone was added to phenyl magnesium bromide it gave but two products, triphenyl carbinol and diphenyl acetaldehyde. From all that had gone before it was quite clear that the aldehyde represented the oxide group but we nevertheless repeated the operation with ethyl magnesium bromide and proved that in this case also the second product is diphenyl acetaldehyde. The action of organic magnesium compounds on a-oxido ketones can, therefore, be represented as follows



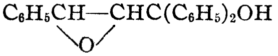
$$(C_6H_5)_2\underbrace{C\text{——}CH}_{O}COC_6H_5 + RMgX \longrightarrow (C_6H_5)_2C{=}CHOMgX + RCOC_6H_5$$

$$C_6H_5\underbrace{CH\text{—}CH}_{O}COC_6H_5 + RMgX \longrightarrow (C_6H_5CH{=}CHOMgX)_N + RCOC_6H_5$$

While these equations accurately represent one phase of the reaction, they leave the process almost as mysterious as before because they supply

[5] Kohler and Johnstin, Am. *Chem. J.*, **33**, 39 (1905).

no adequate reason for the cleavage. These same a-oxido ketones react with substances which, in general, are much more destructive than organic magnesium compounds—ammonia, hydrazine, even alcoholic potassium hydroxide—and the entire molecule reappears in the product; there must therefore be some very special reason for this invariable cleavage by organic magnesium compounds. In a search for this reason the procedure was reversed; a single equivalent of phenyl magnesium bromide was added to an ethereal solution of the oxido ketone at −10° and the mixture was immediately decomposed with iced acid. The result was the oxido carbinol

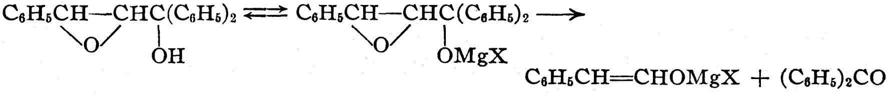


$$C_6H_5\underbrace{CH-CH}_{O}C(C_6H_5)_2OH$$

III

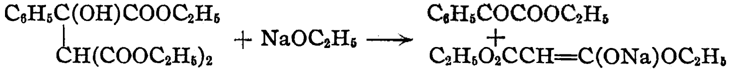
This oxido carbinol can be heated far above its melting point without causing any change and it is not decomposed by methyl alcoholic potassium hydroxide, but when it is added to phenyl magnesium bromide it is promptly cleaved, the final products as usual being triphenyl carbinol and resin. This cleavage is not due to the action of excess of reagent because the oxido carbinol can be made in any desired quantity by adding the oxido ketone to excess of reagent in the usual manner, provided only that the operation is carried out at a sufficiently low temperature and the mixture is decomposed immediately. Moreover, none of the oxido carbinol is obtained when the mixture resulting from the addition of a single equivalent of the reagent is allowed to remain at the ordinary temperature for some time before it is decomposed; it then yields the usual resin and—because no reagent is available for transforming it into triphenyl carbinol—benzophenone.

Thus it has been established, step by step, that cleavage represents the spontaneous decomposition of a magnesium compound which is formed by the addition of one molecule of the reagent to the oxido ketone



$$C_6H_5\underbrace{CH-CH}_{O}\underset{OH}{C}(C_6H_5)_2 \rightleftharpoons C_6H_5\underbrace{CH-CH}_{O}\underset{OMgX}{C}(C_6H_5)_2 \longrightarrow C_6H_5CH=CHOMgX + (C_6H_5)_2CO$$

The magnesium derivative therefore decomposes at temperatures which are more than 100° below those at which the corresponding alcohol is perfectly stable. Some, no doubt, will attribute this great difference in the stability of the carbinol and its magnesium derivative to ionization; others, probably, will find an explanation in chelation. Fundamentally, the cleavage of the carbinol by the addition of an organic magnesium compound is the same as the reversal of an aldol condensation in the presence of alkali, for example[6]



$$\begin{array}{l} C_6H_5C(OH)COOC_2H_5 \\ | \\ CH(COOC_2H_5)_2 \end{array} + NaOC_2H_5 \longrightarrow \begin{array}{c} C_6H_5COCOOC_2H_5 \\ + \\ C_2H_5O_2CCH=C(ONa)OC_2H_5 \end{array}$$

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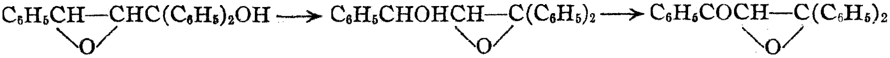
[6] Kohler and Corson, THIS JOURNAL, 45, 1975 (1923).

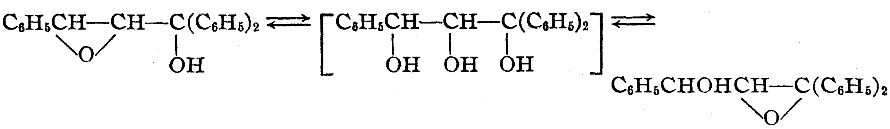
It therefore becomes necessary to consider why alkalies do not produce a corresponding effect on the oxido carbinol. The substance is, in fact, as sensitive to alkalies as it is to Grignard reagents, and alkalies transform it in a manner that is at least as interesting. Thus cold dilute methyl alcoholic potassium hydroxide gradually isomerizes it into an oxido alcohol which still contains an ethylene oxide ring



$$C_6H_5CH{-}CHC(C_6H_5)_2OH \longrightarrow C_6H_5CHOHCH{-}C(C_6H_5)_2 \longrightarrow C_6H_5COCH{-}C(C_6H_5)_2$$

III IV II

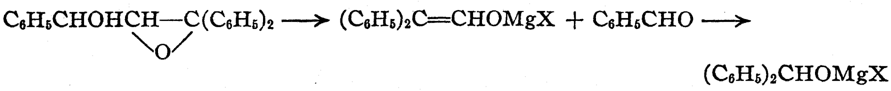
This unexpected isomer gave no little trouble but in the end its structure was established with certainty by oxidation to the oxido ketone II. The process by which this new oxide is formed is probably reversible but it has not as yet been possible to establish this fact with certainty. Since methyl alcoholic alkalies are capable of adding water and methyl alcohol to ethylene oxides, it is conceivable that the rearrangement may occur by way of an open-chained compound



$$C_6H_5CH{-}CH{-}C(C_6H_5)_2 \rightleftarrows \left[\begin{array}{c}C_6H_5CH{-}CH{-}C(C_6H_5)_2\\ OH \quad OH \quad OH\end{array}\right] \rightleftarrows C_6H_5CHOHCH{-}C(C_6H_5)_2$$

But in view of the fact that but one case is known in which it has been possible to convert a glycol into an ethylene oxide,[7] this mechanism seems exceedingly improbable. It is much more likely that the process is similar to that which is responsible for the rearrangement of substituted allyl alcohols, and that the oxide ring offers the same opportunity that is supplied by the double linkage in the alcohol. Whatever the route, the carbinol is rearranged instead of cleaved because, owing to its lack of acidity, it has little tendency to form a potassium compound corresponding to the magnesium derivative.

The product of this rearrangement—the oxido alcohol IV—is by far the most interesting substance that has appeared during the investigation. Like its isomer it can be heated far above its melting point without change, but, as would be expected from what has gone before, it is cleaved by phenyl magnesium bromide and the products in this case are diphenyl acetaldehyde and benzhydrol



$$C_6H_5CHOHCH{-}C(C_6H_5)_2 \longrightarrow (C_6H_5)_2C{=}CHOMgX + C_6H_5CHO \longrightarrow (C_6H_5)_2CHOMgX$$

The oxido alcohol is also very readily cleaved by dilute acids, a process which does not appear to be quite so inevitable as the foregoing, because it occurs under conditions which usually lead to the addition of methyl

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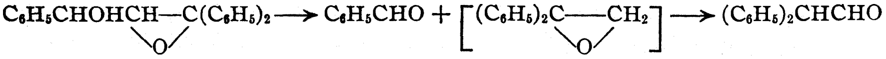
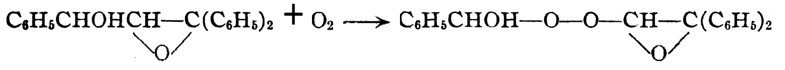
[7] Gardeur, *Bull. acad. roy. med. Belg.*, [3] 34, 67 (1897).

alcohol to an ethylene oxide rather than to the rearrangement of the oxide to an aldehyde



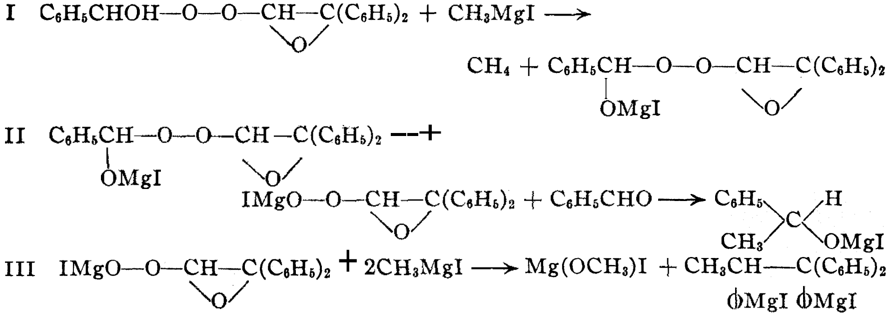
Perhaps the most interesting property of the oxido alcohol is shown in its behavior toward free oxygen. Some preparations appear to undergo no change when they are kept in contact with air in diffused daylight, but others which have been obtained in essentially the same manner undergo autoxidation with sufficient rapidity to produce a perceptible rise in temperature. The process is accompanied by the formation of benzaldehyde and other degradation products, but the principal product is a peroxide which is formed by the insertion of two atoms of oxygen next to the oxide ring.



IV V

The evidence for this strange formula is as follows. When the substance was heated, it decomposed briskly at the melting point and formed benzaldehyde, formic acid and benzophenone

A quantitative analysis with methyl magnesium iodide in isoamyl ether showed that the substance reacted with slightly more than four moles of the reagent and liberated one mole of gas, indicating the presence of one hydroxyl group. When this reaction was repeated in ordinary ether the products were methyl diphenyl glycol—proving the presence of the oxide ring—and methyl phenyl carbinol



These transformations show that the peroxide belongs to a class which heretofore has been obtained only from free radicals or substances which are readily dissociated into free radicals. The problems suggested by its formation are still under investigation but it is clear already that these oxido carbinols and oxido alcohols constitute a remarkable group of substances.

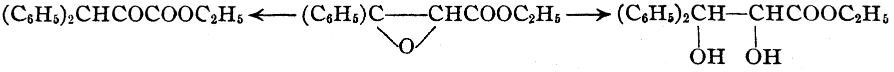
Nothing in the foregoing account suggests the kind of conjugation of the oxido and carbonyl groups that it is necessary to assume in order to explain the results which Bardon and Ramart obtained with diphenyl glycidic ester. We prepared this ester and treated it with phenyl magnesium bromide. Rather to our surprise we found that it was not cleaved. Depending only on the conditions under which the reaction was carried out, it yielded in succession the hydroxy ester VII, the hydroxy ketone VIII and the glycol IX—substances which are manifestly derived from the keto ester VI which is isomeric with the glycidic ester

$$\underset{\text{VI}}{(C_6H_5)_2CHCOCOOC_2H_5} \longrightarrow \underset{\text{VII}}{(C_6H_5)_2CHC(C_6H_5)OHCOOC_2H_5} \longrightarrow$$
$$\underset{\text{VIII}}{(C_6H_5)_2CHC(C_6H_5)OHCOC_6H_5} \longrightarrow \underset{\text{IX}}{(C_6H_5)_2CHC(C_6H_5)OHC(C_6H_5)_2OH}$$

The great rapidity with which the first reaction occurs even in a freezing mixture led to the suspicion that the supposed glycidic ester of Pointet,[8] and of Bardon and Ramart,[4] was in reality the ketonic ester. This proved to be the case because the substance does not combine with water, but readily forms a phenyl hydrazone at the ordinary temperature and is oxidized to diphenyl acetic acid by alkaline hydrogen peroxide

$$(C_6H_5)_2CHC({=}NNHC_6H_5)COOC_2H_5 \longleftarrow (C_6H_5)_2CHCOCOOC_2H_5 \longrightarrow$$
$$(C_6H_5)_2CHCOOH + CO_2 + C_2H_5OH$$

The ester had been prepared by condensing benzophenone with chloro-ethyl acetate both by the method of Pointet and by that of Claisen.[9] The primary product of this condensation is the desired glycidic ester, but this cannot be separated from the unchanged benzophenone. When the mixture is distilled under diminished pressure the glycidic ester is rearranged to the ketonic ester,[10] and when it is distilled with steam the glycidic ester combines with water and forms a glycolic ester



$$\underset{\text{VI}}{(C_6H_5)_2CHCOCOOC_2H_5} \longleftarrow (C_6H_5)C\underset{O}{—}CHCOOC_2H_5 \longrightarrow \underset{\text{X}}{(C_6H_5)_2\underset{OH}{CH}—\underset{OH}{CH}COOC_2H_5}$$

When the crude condensation product—a mixture of the glycidic ester, benzophenone and chloro-ethyl acetate—was added to excess of phenyl magnesium bromide, the product contained diphenylacetaldehyde, showing both that the ester is cleaved in the manner to be expected and also that the products described by Bardon and Ramart are derived from the ketonic ester

$$(C_6H_5)_2CHCOCOOC_2H_5 \longrightarrow (C_6H_5)_2CHC(OH)CH_3COOC_2H_5 \longrightarrow$$
$$(C_6H_5)_2C(OH)CH_3COOH$$

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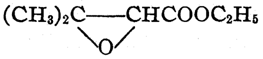
[8] Pointet, *Compt. rend.*, 148, 418 (1909).

[9] Claisen, *Ber.*, 38, 693 (1905).

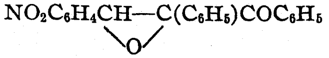
[10] Troell, *ibid.*, 61, 2498 (1928), likewise concluded that distillation converts the glycidic into the ketonic ester but could not induce the latter to crystallize.

Two other substances were treated with phenyl magnesium bromide—an aliphatic glycidic ester and an oxido ketone with a phenyl group in the a-position



$(CH_3)_2C\text{—}CHCOOC_2H_5$ (—O—)

XI



$NO_2C_6H_4CH\text{—}C(C_6H_5)COC_6H_5$ (—O—)

XII

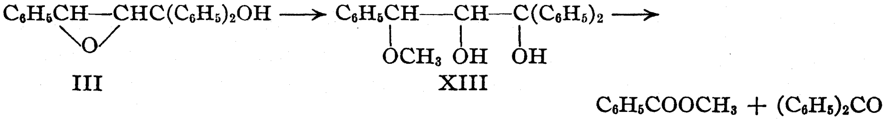
Both gave triphenyl carbinol. There is, therefore, no evidence that any oxido compounds can form 1,4-addition products with organic magnesium compounds.

Experimental Part

I. Experiments with α-Oxido Ketones

Four oxido ketones were treated with organic magnesium compounds for the various reasons specified in the introductory section, but only the reaction between the oxide of benzalacetophenone and phenyl magnesium bromide was studied with care. The structure of the primary product of this reaction was established in the following manner.

An analysis of the substance with methyl magnesium iodide in the machine[11] showed that it contains one hydroxyl group and one other reactive group. In the presence of a little hydrochloric acid the substance combines with methyl alcohol to form a methyl ether which has two hydroxyl groups, but no other group capable of reacting with methyl magnesium iodide; the substance is, therefore, an oxide. The methyl ether formed by addition of methyl alcohol is oxidized by chromic acid to methyl benzoate and benzophenone



$$C_6H_5CH\text{—}CHC(C_6H_5)_2OH \longrightarrow C_6H_5\underset{OCH_3}{CH}\text{—}\underset{OH}{CH}\text{—}\underset{OH}{C}(C_6H_5)_2 \longrightarrow C_6H_5COOCH_3 + (C_6H_5)_2CO$$

III XIII

Moreover, the dihydroxy ether was synthesized by a method recently described by Kohler and Addinall.[12] For this purpose benzalacetophenone dibromide was treated with sodium alcoholate and thus converted into an acetal which was readily hydrolyzed to the corresponding ketone. And when this ketone was treated with phenyl magnesium bromide it gave the same dihydroxy ether that had been obtained from the oxido carbinol

$$C_6H_5CHBrCHBrCOC_6H_5 \longrightarrow \underset{\text{XIV}}{C_6H_5CH(OCH_3)CHOHC(OCH_3)_2C_6H_5} \longrightarrow$$

$$\underset{\text{XV}}{C_6H_5CH(OCH_3)CHOHCOC_6H_5} \longrightarrow \underset{\text{XIII}}{C_6H_5CH(OCH_3)CHOHC(C_6H_5)_2OH}$$

Three of the oxido ketones were prepared by the excellent method of Weitz and Scheffer,[13] but for the preparation of benzalacetophenone oxide,

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[11] Kohler and Richtmyer, This journal, 52, 3736 (1930).

[12] Kohler and Addinall, *ibid.*, 52, 3728 (1930).

[13] Weitz and Scheffer, Ber., 54,2329 (1921).

which was needed in large quantities, the method was modified in the interest of economy and convenience. The procedure is as follows.

Eighty grams of sodium peroxide powder is slowly poured into 650 cc. of cracked ice and water contained in a flask immersed in a good freezing mixture and provided with an efficient motor stirrer; 142 cc. of concentrated (12 normal) hydrochloric acid is then allowed to drop in slowly, stirring vigorously and keeping the temperature below 5° throughout, if necessary by adding a little more cracked ice from time to time. At the end, 50 cc. of alcohol is added.

In the meantime 104 g. (0.5 mole) of benzalacetophenone is dissolved in 2 liters of alcohol and brought to 35° in a beaker supplied with an effective motor stirrer. The cold peroxide solution is at once filtered through glass wool and run into the benzalacetophenone solution with vigorous stirring, in a continuous rapid stream; the addition should be completed within two minutes. Seed is added at intervals until, near the end, the oxide crystallizes rapidly. The yellow color of benzalacetophenone then fades, and the solution becomes practically colorless. The vessel is immersed in a freezing mixture, and stirred slowly until the temperature reaches zero, when the oxide is at once filtered and washed well with cold 60% alcohol; 95 g. of white crystalline oxide, of m. p. 85–90°, is obtained, a yield of 85%. The filtrate contains about 5 or 10 g. more, which is hardly worth recovering. The oxide is easily purified by dissolving in cold acetone, filtering, evaporating to a small volume and adding petroleum ether. The product crystallizes in snow-white flakes, melting at 89–90°. When treated with methyl magnesium iodide in the "machine" it liberates only a negligible amount of gas but consumes two moles of reagent.

Reaction with Ethyl Magnesium Bromide.—To an ethereal solution containing five equivalents of ethyl magnesium bromide was added 35 g. of powdered oxide; stirring was continued at room temperature for forty minutes. The reaction mixture was decomposed with ice and concentrated hydrochloric acid, and the ethereal solution washed, dried and evaporated. Steam distillation left a yellow gummy residue, but the distillate consisted of a colorless oil which was identified by its physical constants and an analysis as diethyl phenyl carbinol. There was obtained 17 g. (66%) of liquid boiling at 110–112° at 20 mm., with n_D^{20} 1.5172. Klages[14] records a boiling point of 107–109° at 14 mm., and n_D^{12} 1.5166.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.5; H, 9.8. Found: C, 80.1; H, 9.6.

Reaction with Phenyl Magnesium Bromide.—When solid benzalacetophenone oxide is added to a solution containing five equivalents of phenyl Grignard reagent at room temperature, heat is evolved, and the solution passes through a characteristic purple stage which we have come to associate with the formation of triphenyl carbinol in reactions of this type. At the end the solution becomes greenish, and a thick, dark-colored gum adheres to the walls of the flask. The solution, upon decomposition with ice and acid, yields large amounts of triphenyl carbinol, while the gum produces mainly a thick yellow sirup which gives no test for phenyl acetaldehyde and has resisted all attempts at depolymerization. The yield of triphenyl carbinol is about 70%.

Preparation of the Oxido **Carbinol, III.—A** Grignard reagent was prepared from 8 g. of magnesium (0.33 mole) and 47 g. (0.30 mole) of bromobenzene in 600 cc. of ether. The filtered solution, in a 3-necked flask equipped with thermometer and, mechanical stirrer, was chilled in a freezing mixture so that its temperature was always below $-10°$. Finely powdered oxide (34 g. = 0.15 mole) was added in the course of thirty minutes, and the mixture stirred for another fifteen minutes. The flask then contained a clear, pale green liquid, arid a gum which contained solid unchanged oxide as well as products

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[14] Klages, *Ber.*, 36, 3692 (1903).

resulting from the action of more than one equivalent of Grignard reagent on the oxide. The liquid was decanted at once into a mixture of ice and concentrated hydrochloric acid; the ethereal layer was washed with several portions of water, dried over calcium chloride, and evaporated to a small volume. Upon dilution with petroleum ether it deposited 22 g. of practically pure product.

If prepared by the inverse method, the procedure was as follows. Into a solution of 15 g. of oxide in 800 cc. of dry ether kept at $-10°$ was allowed to dribble one equivalent of phenyl magnesium bromide during the course of an hour. A yellowish white solid appeared. After another hour's stirring in the freezing mixture the contents of the flask were poured on iced acid and the ethereal layer treated as before. There was obtained 9 g. of pure product, besides some unchanged oxide and a rather unstable halogen compound which was not further investigated.

When a similar solution was allowed to stand at room temperature overnight instead of being decomposed immediately upon removal from the freezing mixture, no primary product could be isolated. Some yellowish white magnesium derivative was filtered and decomposed separately; it yielded the unstable halogen compound, melting at about 100° with vigorous decomposition. The filtrate, after being decomposed, was subjected to steam distillation. Much benzophenone was obtained, and the gummy polymer remained in the flask. From this and other observations we may conclude that cleavage of the primary magnesium derivative is not due to excess of Grignard reagent.

α-Phenyl-β-(diphenyl-hydroxy-methyl) Ethylene Oxide, 111.—The product obtained by the above procedures is very soluble in ether, moderately soluble in methyl alcohol, and difficultly soluble in petroleum ether. From a mixture of ether and petroleum ether it separates in clusters of large needles which melt at 129–130°. With methyl magnesium iodide it liberated 1.0 mole of gas and consumed 2.1 moles of reagent.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.7; H, 5.9.

With excess phenyl magnesium bromide at $-10°$ for one hour, most of the substance was recovered unchanged; at room temperature, however, triphenyl carbinol was the only product which could be isolated. A sample maintained for one hour at 150° showed no evidence of decomposition, and the melting point was unaffected. The compound was not attacked by acetic anhydride, even on warming and allowing the solvent to evaporate over caustic alkali in a vacuum desiccator. Concentrated ammonium hydroxide alone, or in methyl alcohol, was also without effect.

Addition of Methyl Alcohol: **α,α,γ-Triphenyl-α,β-dihydroxy-γ-methoxy** Propane, **XIII.**—A solution of 5 g. of the primary product III in 70 cc. of absolute methyl alcohol containing 10 drops of concentrated hydrochloric acid was boiled for one hour. Dilution with water precipitated an oil which smelled strongly of benzaldehyde, but which deposited a mass of crystals when petroleum ether was added. The solid was filtered and washed with petroleum ether. The petroleum ether solution was concentrated and distilled with steam; the first fractions contained benzaldehyde, the latter fractions diphenylacetaldehyde, which was identified through its semicarbazone melting at 158–160" by comparison with a specimen at hand.

The solid can be obtained in much better yield by shaking at room temperature, thereby avoiding the destructive cleavage to benzaldehyde and diphenylacetaldehyde. The product is moderately soluble in acetone and ether, sparingly soluble in petroleum ether; it crystallizes from ether in clusters of prisms which melt at 154–155°. With methyl magnesium iodide it evolved 2.0 moles of gas and consumed 2.1 moles of reagent. Oxidized with chromic acid in glacial acetic acid it yielded methyl benzoate and benzophenone, identified by the odor and mixed melting point, respectively

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.0; H, 6.6. Found: C, 78.3; H, 6.9.

Independent Synthesis of the Dihydroxy Ether: The Dimethyl Acetal of a-Hydroxy-β-methoxy-β-phenyl Propiophenone, XIV.—To a solution of 22 g. of sodium in 500 cc. of dry methyl alcohol which was cooled in a freezing mixture was added 170 g. of pure solid benzalacetophenone dibromide. The mixture was allowed to remain in the freezing mixture for five hours, then kept at nearly 0° in a refrigerator for three days. By this time all of the solid dibromide had disappeared but the very pale yellow solution was still slightly alkaline.

The solution was allowed to evaporate in an open dish. It left a residue composed of sodium bromide and colorless needles of an organic compound imbedded in a large quantity of pale yellow oil. This residue was dissolved in ether and water. The ethereal layer was thoroughly washed with water, dried over sodium sulfate, concentrated, and inoculated with the needles previously obtained. It gradually deposited 24 g. of the solid acetal, and 5 g. more was obtained by diluting the oily filtrate with low-boiling petroleum ether, and cooling it in a freezing mixture. The solid was thoroughly washed with petroleum ether and then recrystallized from dry methyl alcohol, from which it separates in stubby prisms with a brilliant luster. The melting point is 122". It is readily soluble in ether and acetone, moderately soluble in methyl alcohol, sparingly soluble in petroleum ether.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.5; H, 7.3. Pound: C, 71.2; H, 7.4.

Hydrolysis, Followed by Reaction with Phenyl Magnesium Bromide.—The acetal group is readily hydrolyzed to the corresponding ketone by dilute acid. Thus, 9 g. of acetal was shaken with 200 cc. of dry methyl alcohol containing 3 cc. of concentrated hydrochloric acid. After ten minutes the solution was diluted with water and extracted with ether. The ethereal solution was thoroughly washed with water, dried over calcium chloride to remove the last traces of water and alcohol, and evaporated to about 100 cc.

Since a preliminary experiment had failed to produce a crystalline ketone, the ethereal solution itself was added to an excess of phenyl magnesium bromide. A white precipitate formed and redissolved. The mixture was boiled gently for fifteen minutes and then poured into ice and hydrochloric acid. The ethereal layer deposited 8 g. of the dihydroxy ether—a quantitative yield.

Isomerization of the Oxido Carbinol: α,α-Diphenyl-β-(hydroxy-benzyl) Ethylene Oxide, IV.—A solution of 0.8 g. of potassium hydroxide in 2 cc. of water was added to a solution of 20 g. of the oxido carbinol in 400 cc. of methyl alcohol. The mixture was shaken for two days, during which all of the carbinol dissolved. One-fourth of the solution was then gradually diluted with ice water while the walls of the vessel were rubbed with a glass rod. It precipitated the new oxide in small prisms, hexagonal in outline, along with some unchanged oxido carbinol. Whether the latter was due to incomplete reaction or whether it indicates that the process is reversible has not yet been established. The yield of pure isomer from one-fourth of the solution was at least 3 g.

The new compound is very soluble in alcohol and in ether, sparingly soluble in petroleum ether. After two recrystallizations from ether–petroleum ether, the melting point was constant at 103°. The substance was recovered unchanged after being heated to 150°. In the machine it liberated 0.9 mole of gas and consumed 2.1 moles of reagent.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.3; H, 6.2.

Oxidation to Benzoyl Diphenyl Ethylene Oxide 11.–A portion of the isomer was added to a warm solution of one equivalent of chromic acid in glacial acetic acid. As the mixture became green instantly, it was poured at once into water. The ethereal extract, after being washed with water and sodium carbonate, and dried over calcium chloride, was concentrated to a small volume. Crystals of the ketonic oxide, II, separated, and were identified by a mixed melting point with this substance, which is to be described later.

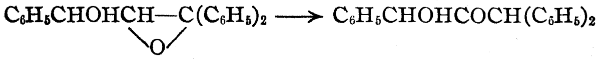
Reaction with Phenyl Magnesium Bromide.—The product from 2 g. of the oxido alcohol, after treating with an excess of phenyl Grignard reagent, was a yellowish mobile oil which showed no tendency to solidify. A fractional distillation with steam enabled us to separate first a diphenyl fraction; then an intermediate fraction containing diphenylacetaldehyde, which was identified as the semicarbazone; and finally benzhydrol, which crystallized in the aqueous distillate in fine needles, and was identified by a mixed melting point.

Reaction with Methyl Magnesium Iodide (Inverse).—A solution of 3 g. of the freshly recrystallized alcohol in absolute ether was cooled in ice and treated with 1.25 equivalents of methyl magnesium iodide. The mixture, which contained a yellow precipitate in a pale red solution, was boiled for twenty minutes and then decomposed with iced acid. The ethereal layer was washed with thiosulfate and water, evaporated, and fractionally distilled with steam. In the first fraction benzaldehyde was identified by its odor and by conversion into the phenyl hydrazone. In the last fraction diphenyl acetaldehyde was identified by means of its semicarbazone melting at 160–161°.

The residue left in the distilling flask was dissolved in ether. The dried ethereal solution deposited 0.7 g. of a sparingly soluble solid which crystallized from acetone–petroleum ether in needles melting at 128°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 60. Found: C, 83.4; H, 6.1.

According to the analysis this is still another isomer of oxido carbinol. In the "machine" it reacted with 2.2 moles of reagent and liberated 1.8 moles of gas, and it was recovered unchanged. Since it was neither affected by hydrochloric acid in methyl alcohol nor cleaved by methyl magnesium iodide, it is presumably an a-hydroxy ketone formed during the steam distillation from unchanged oxido alcohol



$$C_6H_5CHOHCH\underset{\diagdown O \diagup}{—}C(C_6H_5)_2 \longrightarrow C_6H_5CHOHCOCH(C_6H_5)_2$$

Autoxidation: The Peroxide, V.—A batch of 8.2 g. of the oxido alcohol freshly recrystallized from ether and petroleum ether was placed in a small glass dish covered with a watch glass. In the course of three hours, it developed a perceptible temperature and a strong odor of benzaldehyde. It was left to itself for five days and then well washed with ether. The residue—5 1 g.—was recrystallized from acetone. It separated in fine needles, sparingly soluble in alcohol, ether and acetone. It melts at about 160° with brisk decomposition.

Anal. Calcd. for $C_{21}H_{18}O_4$: C, 75.5; H, **5.4.** Found: C, 75.3; H, 5.6.

In the machine, 1 mole of the substance consumed 4.2 moles of reagent and liberated 1 mole of gas.

Thermal Decomposition.—One and one-half grams of the peroxide was distributed in eight boats placed end to end in a combustion tube. As each boat was heated at one point until the peroxide melted, decomposition started and spread through the boat. The decomposition products were collected in ether. From the ethereal solution water extracted formic acid, which was identified by its reducing action on mercuric oxide.[15] The ethereal solution was fractionally distilled with steam; the first fraction contained benzaldehyde—identified as its phenyl hydrazone—the later fractions benzophenone, which was identified by its melting point before and after mixing with a sample.

Reaction with Methyl Magnesium Iodide.—To a solution of methyl magnesium iodide containing 1 g. of magnesium was added 1.8 g. of the peroxide in the form of a finely ground solid. The solid dissolved with evolution of gas and precipitated a gum which disappeared after prolonged stirring. The clear colorless solution was then de-

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[15] **Mulliken,** "Identification of Pure Organic Compounds," 1914, p. 83.

composed with iced acid, the ether extract washed with thiosulfate and water, dried and concentrated. It deposited a solid which after recrystallization from ether–petroleum ether melted at 94–95".

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 79.0; H, 7.0 Found: C, 78.8; H, 7 1.

In the machine one mole of the substance reacted with two moles of methyl magnesium iodide, liberated two moles of gas, and was recovered after addition of water.

The composition, crystalline form and melting point indicated that the substance was diphenyl methyl glycol. This glycol was therefore synthesized by treating ethyl lactate with excess of phenyl magnesium bromide. A comparison of the two products proved their identity.

The mother liquors from the glycol, on evaporation, left an oil. From the amount of reagent consumed it was to be expected that this oil contained methyl phenyl carbinol. It was therefore oxidized with a slight excess of chromic acid in glacial acetic acid. The oxidation product, isolated in the usual manner, was acetophenone. It was identified by condensing it with m-nitro benzaldehyde and comparing the condensation product with a sample of m-nitro benzalacetophenone.

Preparation of Benzoyl Diphenyl Ethylene Oxide: **α-Bromo-β,β-diphenyl-β-hydroxy Propiophenone, I.**—To an ice-cold Grignard reagent prepared from 24 g. of magnesium and 140 g. of bromo benzene was added 85 g. of dibromo dibenzoylmethane. Considerable heat was evolved and a transient yellow color appeared with each addition of solid. After fifteen minutes' stirring at the ordinary temperature the mixture was poured into iced acid, and the precipitated bromohydrin filtered and washed with ether, in which it is sparingly soluble. For analysis a small sample was purified by recrystallization from chloroform and petroleum ether, from which it separated in colorless, rectangular plates. It melts, with effervescence, at about 180°.

Anal. Calcd. for $C_{21}H_{17}O_2Br$: C, 66.2; H, 4.5. Found: C, 66.3; H, 4.4.

Benzoyl Diphenyl Ethylene Oxide, II.—A methyl alcoholic solution of sodium methylate was added to a suspension of the bromohydrin until the solution was slightly alkaline and the yellow color permanent; the suspended material now consisted of the oxido ketone and sodium bromide. The mixture was acidified with *a* little acetic acid, the product collected on a filter, washed with methyl alcohol and water, and recrystallized from acetone. It separated in clusters of short acicular prisms and melted at 124–125°. It is sparingly soluble in cold ether, alcohol and acetone. The yield was very nearly quantitative.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5 3. Found: C, 84.2; H, 5.6.

With methyl magnesium iodide the oxide consumed two moles of reagent and liberated only a negligible quantity of gas

Reaction with Phenyl Magnesium Bromide.—Heat was evolved and a reddish-purple color developed when *2* g. of oxide was added to excess phenyl Grignard reagent at room temperature. The color soon faded to a light green, and after fifteen minutes the solution was decomposed with ice and acid. The ethereal solution, after being washed with water and dried over sodium sulfate, was concentrated, whereupon it deposited 0.8 g. of triphenyl carbinol The residue was distilled with steam; from the middle fractions, treated with semicarbazide hydrochloride and sodium acetate in alcohol, was obtained the semicarbazone of diphenyl acetaldehyde, melting at 158–160°. Nixed with a known sample it melted at 158–161°.

Reaction with Ethyl Magnesium Iodide.—The oxide was treated in the same way with an excess of ethyl Grignard reagent. The ethereal solution, after concentration, was distilled with steam, and diphenyl acetaldehyde identified in the second half of the distillate.

Reaction with Other Oxido Ketones.—The experiments with the oxides of benzalacetone, anisalacetophenone, and α-phenyl-*p*-nitrobenzalacetophenone need not be described in detail because, as explained in the introduction, they were performed for special reasons and the general procedure was the same as that which has been described under the oxide of benzalacetophenone.

II. Experiments with Glycidic and Glyoxylic Esters

At first we prepared glycidic esters by the very convenient method of **Claisen**,[9] but found that the products contained considerable quantities of acid amides, which complicated still further the problem of isolating pure substances. We therefore turned to the method of **Darzens**.[16] For the preparation of diphenyl glycidic ester the procedure was as follows.

Into a well-cooled mixture of 182 g. of benzophenone and 122.5 g. of chloro-ethyl acetate, 68 g. of finely divided dry sodium ethylate was introduced at such a rate that the temperature could be kept below 5°. The mixture was allowed to remain at room temperature for twelve hours, then heated to 100° for six hours. After acidification with acetic acid it was diluted with water, which dissolved the salts and precipitated the oily ester. This was extracted with ether, the ethereal solution washed and dried. A small portion of the ethereal solution, evaporated at this stage, left a residue of 4.8 g. of an oil which when distilled with steam yielded 3.9 g. of diphenyl glycolic ester, showing that about 75% of the ketone had been converted into the glycidic ester.

The rest of the ethereal solution was fractionally distilled under a pressure of 3–10 mm. The fraction boiling at 190° was again examined by distillation with steam. It contained some benzophenone, which appeared in the distillate, but no sparingly soluble glycolic ester could be found in the residue. Distillation therefore destroys the oxido ester.

Reaction with Phenyl Magnesium Bromide.—Since it was impossible to isolate the pure oxido ester, an ethereal solution of the crude ester was added to a large excess of phenyl magnesium bromide in the customary manner. The product was manipulated in the usual manner and the residue left after removing triphenyl carbinol was distilled with steam. The first fractions contained diphenyl, the later fractions diphenyl acetaldehyde, which was identified as its semicarbazone. The a-oxido ester, therefore, does not give products of the type described by Bardon and Ramart but is cleaved like the oxido ketones.

Diphenyl Glyoxylic Ester, VI.—Since the oil obtained by distilling the crude glycidic ester failed to solidify in a freezing mixture, a small quantity of it was hydrolyzed by the method of Pointet? The resulting sodium salt was converted into the silver salt, and from the silver salt the ester was regenerated by boiling it for three hours with ethyl iodide. The ester obtained in this manner was a solid. Large quantities of this same solid ester were then obtained by diluting the remainder of the oily distillate with ether and petroleum ether, cooling the solution in a freezing mixture and inoculating it with the solid. After repeated recrystallization from ether and petroleum ether the ester melted at 37°, and this melting point remained constant during five consecutive crystallizations. Pointet reported a melting point of 47°, but either this is a typographical error or else as Troell suggests Pointet's solid was benzophenone.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.2; H, 6.2.

The ester crystallizes in prisms which are readily soluble in alcohol and in ether, moderately soluble in petroleum ether. With methyl iodide it evolved 0.3 mole of gas,

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[16] Darzens, *Comfit. rend.*, 139, 1214 (1904); 141,766 (1905).

indicating a tendency toward enolization similar to that of phenyl benzhydryl ketone. In order to prove that the substance is in reality a glyoxylic ester, it was turned into a phenyl hydrazone and oxidized with alkaline hydrogen peroxide.

Phenylhydrazone.—A solution of the ester in alcohol containing phenyl hydrazine hydrochloride deposited the phenyl hydrazone at the ordinary temperature within half an hour. The hydrazone is moderately soluble in ethyl alcohol, from which it separates in yellow prisms melting at 99–100°.

Anal. Calcd. for $C_{23}H_{22}O_2N_2$: C, 77.1; H, 6.1. Found: C, 77.4; H, 6.3.

Oxidation.—To a solution of 1 g. of ester and 3 cc of 20% hydrogen peroxide in 25 cc. of ethyl alcohol, dilute aqueous sodium hydroxide was added drop by drop during the course of an hour until somewhat more than one equivalent had been added. After another hour the solution was diluted with water and extracted with ether to remove any unchanged ester. The alkaline solution was acidified and extracted with ether; the latter was washed with water, dried with calcium chloride and evaporated. The residue, crystallized from ether–petroleum ether, melted at 145–146°; diphenyl acetic acid melts at 146° (Pointet).

Saponification: Phenylhydrazone of Diphenyl Glyoxylic Acid.—As a control for the above oxidation, 1 g. of ester was treated in the same way in the absence of hydrogen peroxide and another acid melting at 110–115° obtained. This is diphenyl glyoxylic acid, of melting point 116° (Pointet), and not diphenyl glycidic ester as Pointet believed. It readily forms an alkali-soluble phenyl hydrazone which crystallizes from hot methyl alcohol in yellow needles and melts with decomposition at about 210° (when heated slowly) or at about 245' (instantaneously on a block).[17]

And. Calcd. for $C_{21}H_{18}O_2N_2$: C, 76.4; H, 5.4. Found: C, 76.4; H, 5.1.

The Methyl Ester: $(C_6H_5)_2CHCOCOOCH_3$.—The methyl ester was prepared in the hope that the methyl ester of phenyl glycidic acid—formed by condensing benzophenone with methyl chloro-acetate—might be obtained as a solid. All attempts to induce the crude condensation product to solidify were unsuccessful and distillation rearranged the glycidic into the glyoxylic ester. In order to get the latter to crystallize it likewise was necessary to secure a small quantity of solid for inoculation by methylating the acid through the silver salt. The ester boils at 175° under 5 mm., crystallizes from methyl alcohol in prisms, and melts at 75°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.5. Found: C, 75.8; H, 5.7.

Reaction with Phenyl Magnesium Bromide.—The reaction between the ethyl ester of diphenyl glyoxylic acid and phenyl magnesium bromide was investigated by Bardon and Ramart,[4] who thought, however, that they were dealing with the glycidic ester. They reported an ester alcohol melting at 130° and another product melting at 203–205' but identified neither of these substances.

Ethyl **α,β,β-Triphenyl-α-hydroxy** Propionate, **VII.**—An ethereal solution of 10 g. of the glyoxylic ester was added to an excess of phenyl magnesium bromide in an ice-bath, and the mixture was immediately poured into iced acid. The ethereal layer yielded 8 g. of a solid product and a small quantity of oil. A better yield (10 g.) of the same product was obtained by operating in an inverse manner. The hydroxy ester is moderately soluble in ether, from which it separates in nodules of minute needles melting at 118–120°.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 70.7; H, 6.4; OC_2H_5, 13.0. Found: C, 79.5; H, 6.4; OC_2H_5, 13.7.

α,β,β-Triphenyl-α-hydroxy Propiophenone, VIII, and **α,α,β,γ,γ-Pentaphenyl-α,β-**dihydroxy Propane, **IX.**—These two substances are always formed together when either

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[17] *Cf.* Troell, Ref. 10, p. 2502, who gives 189° with decomposition.

the glyoxylic ester or the monohydroxy ester VII is added to a large excess of phenyl magnesium bromide, and the mixture is either allowed to remain for several days at the ordinary temperature or boiled for three or four hours, before it is decomposed with iced acid. In order to separate the mixture successfully it is necessary to proceed with great caution because the dihydroxyl compound is very readily cleaved into four other products, and when this happens the separation is almost hopeless. The most satisfactory procedure was as follows. A solution obtained by adding 20 g. of the hydroxy ester VII to an excess of phenyl magnesium bromide was boiled for three hours, then diluted with twice its volume of low-boiling petroleum ether and cooled in a freezing mixture for several hours. The top layer was treated separately with iced acid, but it contained little besides diphenyl and excess of phenyl magnesium bromide. The bottom layer was mixed with fresh ether, then likewise decomposed with iced acid. The ethereal solution was washed and dried, then allowed to evaporate in an open vessel. It left a pale yellow oil.

The oil was repeatedly extracted with low-boiling ether until the undissolved portion finally solidified. The solid was recrystallized from acetone and methyl alcohol and was thus readily purified. It crystallized in long truncated columns melting with decomposition at about 190°.

Anal. Calcd. for $C_{33}H_{28}O_2$: C, 86.8; H, 6.2. Found: C, 86.7; H, 6.3.

This substance is the glycol IX, as was established in the following manner. When it was treated with methyl magnesium iodide in the machine, it consumed two moles of reagent and liberated two moles of gas; therefore it contains two hydroxyl groups. When its solution in ethyl alcohol or, better, glacial acetic acid, was boiled for a few hours it decomposed, cleanly, into phenyl benzhydryl ketone and benzhydrol—both isolated and identified by comparison with samples in hand. And when it was kept a few degrees above its melting point for a short time it gave in addition to the two products already mentioned, smaller quantities of triphenyl ethyl alcohol and benzophenone, which were separated by fractional steam distillation and likewise identified by comparison with authentic samples.

$$\text{I}\quad (C_6H_5)_2CHC(C_6H_5)OHC(C_6H_5)_2OH \longrightarrow (C_6H_5)_2CHCOC_6H_5 + (C_6H_5)_2CHOH$$

$$\text{II}\quad (C_6H_5)_2CHC(C_6H_5)OHC(C_6H_5)_2OH \longrightarrow (C_6H_5)_2CHCHOHC_6H_5 + (C_6H_5)_2CO$$

The petroleum ether extracts were allowed to evaporate spontaneously. They gradually deposited along with a small quantity of the glycol another solid which separated in flat needles and after recrystallization from ether–petroleum ether melted at 123°.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.7; H, 5.8. Found: C, 85.7; H, 6.1.

This substance must be the hydroxy ketone VIII, because when it was boiled for three hours with a slight excess of phenyl magnesium bromide it was converted into the glycol IX.

The Glycolic Ester, X.—As was stated earlier, the crude glycidic ester, when distilled with steam, left a residue which solidified during the distillation. The solid was recrystallized from alcohol in fine lustrous needles melting at 130°.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.3; H, 6.3. Found: C, 71.6; H, 6.5.

The corresponding methyl ester, obtained in a similar manner, likewise crystallized in silky needles and melted at almost the same temperature as the ethyl ester, 130–131°. A mixture of the two, however, melted at 110°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.6; H, 5.9. Found: C, 70.8; H, 5.9.

Summary

1. When organic magnesium compounds react with α-oxido ketones, they combine with the carbonyl group only. By operating at a low tem-

perature and decomposing the product immediately, it is possible to secure the corresponding oxido carbinol; otherwise, the unstable magnesium derivatives decompose spontaneously into magnesium derivatives of aldehydes, and ketones which may subsequently be transformed into tertiary alcohols.

2. Organic magnesium derivatives first transform α-oxido esters into a-oxido ketones; the final products are therefore the same as those obtained with these ketones. Other results have been reported but the substance used in these cases was an a-ketonic ester and not the supposed isomeric α-oxido ester.

3. Oxido carbinols are reactive substances which show unexpected properties.

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CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OP ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 60]

STUDIES IN AUTO-OXIDATION REACTIONS. II. THE MECHANISM OF THE AUTO-OXIDATION OF CERTAIN ETHERS

BY NICHOLAS A. MILAS[1]

RECEIVED SEPTEMBER 22, 1930 PUBLISHED JANUARY 12, 1931

Introduction

In previous publications[2] from this Laboratory a general theory has been advocated, which, if properly applied, seems to account for the various phenomena and mechanism of auto-oxidation reactions. Briefly stated, the theory assumes the addition of molecular oxygen to compounds containing molecular valence electrons comparable to valence electrons of atoms. As a direct consequence of this theory, one would expect molecular oxygen to add directly onto the bivalent oxygen atom present in alcohols, ethers, ketones, aldehydes, etc., or onto the bivalent sulfur atom present in thio-alcohols, thio-ethers, thio-phenols, thio ketones, etc., or onto the trivalent nitrogen atom present in primary, secondary and tertiary amines, hydrazones and the like to form highly unstable dative peroxides which either rearrange or hydrolyze to yield other relatively more stable peroxides. Certain ethers were chosen for the present investigation because of the existence of diversity of opinion regarding the fundamental mechanism of their auto-oxidation.

The auto-oxidation of ethyl ether has been the subject of several investigations of which only two will be mentioned here. Clover[3] was the

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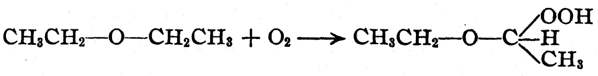
[2] Milas, **(a) J.** *Phys. Chem.*, **33,1204** (1929); (b) THIS JOURNAL, **52,739 (1930).**

[3] **Clover,** *ibid.*, **44,** 1107 (1922).

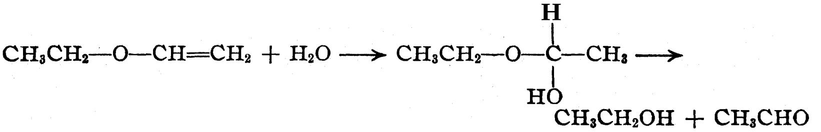
first to make a serious attempt to elucidate the mechanism of the auto-oxidation of ethyl ether. He proposed the mechanism



$$CH_3CH_2{-}O{-}CH_2CH_3 + O_2 \longrightarrow CH_3CH_2{-}O{-}C\begin{cases}OOH\\H\\CH_3\end{cases}$$

which was based on his claim to have isolated an ether peroxide having acidic properties. This claim, however, was later disputed by Wieland and Wingler,[4] who attributed the peroxidic properties of ethyl ether to "dioxy-ethylperoxide," which is assumed to be an addition product of one molecule of hydrogen peroxide to two molecules of acetaldehyde. To reconcile the oxidation of ethyl ether with Wieland's early views[5] on oxidation, Wieland and Wingler proposed a primary dehydrogenation of ethyl ether followed by the formation of hydrogen peroxide and vinyl ethyl ether with subsequent hydrolysis of the latter to form alcohol and acetaldehyde.

$$CH_3CH_2{-}O{-}CH_2CH_3 + O_2 \longrightarrow CH_3CH_2{-}O{-}CH{=}CH_2 + H_2O_2 \qquad (1)$$



$$CH_3CH_2{-}O{-}CH{=}CH_2 + H_2O \longrightarrow CH_3CH_2{-}O{-}\underset{HO}{\overset{H}{C}}{-}CH_3 \longrightarrow CH_3CH_2OH + CH_3CHO \qquad (2)$$

However, the dehydrogenation mechanism, as applied to the oxidation of ethers, seems to be in direct conflict with experimental evidence. It has already been shown elsewhere[2]" that the dehydrogenation theory is incapable of explaining true auto-oxidation reactions. The question, therefore, remains whether the oxidation of ethers fulfils the criteria of auto-oxidation reactions. This is answered in the affirmative in the experimental portion of this paper. The auto-oxidation of dibenzyl ether, for example, was found not only to be appreciably influenced by both negative and positive catalysts, but also to be capable of inducing the oxidation of substances otherwise inert to molecular oxygen.

Furthermore, the isolation of active organic peroxides from the oxidation of ethers makes the reaction of "active" hydrogen with molecular oxygen, rather than with these peroxides, very improbable. These peroxides, without doubt, ought to be far better hydrogen acceptors than molecular oxygen, since they liberate iodine instantly from a neutral solution of potassium iodide, which is relatively stable to molecular oxygen.

Besides, if vinyl ethers were to form during the oxidation of ethers, one would expect them to be oxidized by the active peroxides or peracids formed, leading to oxidation products different from those ordinarily found. Bergmann and Miekeley[6] have shown that vinyl ethyl ether is

[4] Wieland and Wingler, *Ann.*, 431, 317 (1923).

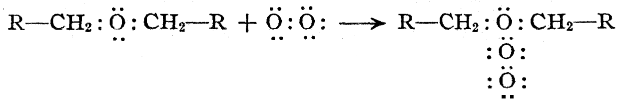
[5] Wieland, Ber., 45, 484, 685, 679, 2603 (1912).

[6] Bergmann and Miekeley, *ibid.*, 54, 2151 (1921).

easily oxidized by benzoperacid to a crystalline substance which hydrolyzes, in presence of mineral acids, to glycolic aldehyde and ethyl alcohol. No glycolic aldehyde has ever been isolated from the oxidation of ethyl ether.

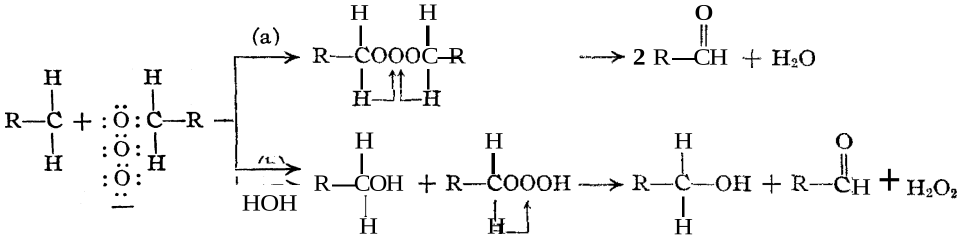
Finally, we have found that tertiary butyl methyl, tertiary butyl benzyl, dibenzyl and methyl cresol ethers, 1,4-dioxane, anisole and even diphenyl ether form peroxides upon oxidation, yet it is quite difficult to conceive a dehydrogenation mechanism for these oxidations.

One may very reasonably conclude, therefore, that the oxidation of ethers with molecular oxygen is a true auto-oxidation phenomenon, which, according to our view, should proceed through the primary addition of molecular oxygen onto the bivalent oxygen atom of the ethers, and could be expressed in general



$$R{-}CH_2:\ddot{\underset{..}{O}}:CH_2{-}R + \ddot{\underset{..}{O}}:\ddot{\underset{..}{O}}: \longrightarrow \begin{array}{c} R{-}CH_2:\ddot{O}:CH_2{-}R \\ :\ddot{O}: \\ :\ddot{\underset{..}{O}}: \end{array}$$

Such a dative or oxonium peroxide would be extremely unstable, but not improbable, since there exists considerable chemical evidence[7] to indicate that the oxygen atom in ethers is relatively unsaturated and can readily form oxonium compounds. The addition of molecular oxygen to ethers, as shown above, will induce a positive charge on the ether oxygen which will then have the tendency to attract toward it the electrons from the neighboring carbon atoms, leaving at least one of them positively charged. This displacement of electrons will cause a weakening of one of the linkages between the carbon atom and the ether oxygen, leading to the following possible changes



These reactions seem to account adequately for the initial products formed in the auto-oxidation of ethers. Reaction (b) seems to predominate although reaction (a) is indispensable to account for the products of reaction (b) appearing in the oxidation of very dry ethers.

The organic peroxide shown in reaction (b) seems to be identical with the primary peroxide formed in the auto-oxidation of alcohols.[8] More-

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[7] Ghosh, *J. Chem. Soc.*, **107,** 1789 (1915). For a somewhat complete bibliography on oxonium salt formation of ethers, see Rigby, Ph.D. Dissertation, M. I. T., June, 1930.

[8] Milas, unpublished results.

over, peroxides of this type exhibit properties similar to monoxyalkyl peroxides prepared by Woker[9] by mixing either formaldehyde or acetaldehyde with hydrogen peroxide preferably in the ratio of 1:1. This mixture yields with benzidine a blue color which is characteristic and is not produced by either the aldehyde or hydrogen peroxide separately. Quite recently King[10] has advanced the view that in deteriorated diethyl ether the main substance responsible for the peroxidic properties is monoxyethyl peroxide. Furthermore, our own experiments indicate that monoxyalkyl peroxides are formed as the primary decomposition products in the oxidation of ethers. These peroxides can further combine with free aldehydes to form dioxy-alkyl peroxides previously described by Nef[11] and by Wieland and Wingler.[4]

It may be mentioned here that during the oxidation of ethers side reactions seem to occur, which are responsible for the production of small quantities of esters and acids. These will not be considered in the present paper.

Experimental Part

The experimental part of this paper is divided into two sections: the first dealing with the oxidation of dibenzyl ether under the influence of various catalysts and the second with the oxidation of various ethers under the influence of ultraviolet radiation.

(1) Oxidation of Dibenzyl Ether.—This ether was chosen because preliminary experiments revealed that it has a higher rate of oxidation than any of the other ethers studied.[12] Moreover, the oxidation of this ether cannot be easily interpreted on the basis of the dehydrogenation theory.

The dibenzyl ether used was the C. P. quality furnished by the Eastman Kodak Company. This was further purified by shaking first with sodium carbonate solution to remove any benzoic acid present, then with sodium bisulfite containing potassium iodide to remove both the aldehyde and the peroxide present in the ether. The ether was finally washed with water, dried over anhydrous sodium sulfate and fractionated under reduced pressure in an atmosphere of pure nitrogen; the fraction boiling at 149.5 to 151.5° under 7 mm. pressure was collected and stored in a brown bottle under an atmosphere of nitrogen.

The experiments were performed in a shaking thermostat[13] at 40 ± 0.05°, and at a shaking speed of 248 complete strokes per minute. The thermostat consists of a Stanley insulated gallon jug fitted with a device in such a way as to permit thermoregulation while the thermostat is being shaken. This device (Fig. 1) consists of a coiled steel

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[9] Woker, *Z. allgem. Physiol.*, **16, 340 (1914); Ber., 47, 1024 (1914).**

[10] King, **J. *Chem. Soc.*, 738 (1929).**

[11] Nef, **Ann., 298, 292 (1897).**

[12] Except tertiary butyl benzyl, which was prepared long after the experiments had been performed with dibenzyl ether.

[13] This was built for the author by Mr. C. L. Gallagher of the Research Laboratory of Physical Chemistry.

tube of 0.8 mm. internal diameter about 36 cm. long and contains sixteen loops. On one end it is welded directly onto a steel mercury well which is fastened inside the thermostat, and on the other end, it is cemented to a capillary glass tube thereby permitting the necessary connections with the relay, etc.

Before each experiment the apparatus was evacuated by closing stopcocks 2 and 3; oxygen, which had been previously dried by passing it through concd. sulfuric acid and phosphorus pentoxide, was allowed to fill the entire apparatus, then by means of a 10-cc. calibrated pipet the sample of the ether (10.36 g.) was dropped into the reaction chamber by removing the ground-glass stopper A. The apparatus was once again evacuated, refilled with oxygen and the reaction allowed to proceed. The total oxygen absorption at any given time was corrected to standard conditions, then changed to cc. per mole of the ether. Figure 2 shows the total oxygen absorption per mole as plotted against time, while Fig. 3 shows the average oxygen absorption rate against time. The results of the experiments with picric acid and *p*-benzoquinone as negative catalysts are not shown on the plots because the absorption was so small that it was impossible to read it without making a large percentage of error. For the sake of comparison the total volume of oxygen absorbed in each experiment at the end of a period of 120 hours, and the total peroxide found expressed both in cc. of 0.02 N thiosulfate and in peroxide oxygen per mole of the ether are given in Table I. It may be seen that the total peroxide oxygen is only a small part of the total oxygen absorbed. This is due to the fact that comparatively large amounts of benzaldehyde and benzoic acid are also formed, which account for the total oxygen absorbed.

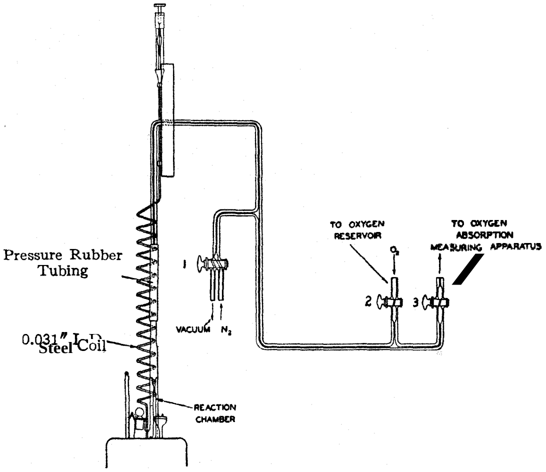

Fig. 1.—Diagram of flexible connection to shaking apparatus for oxygen absorption measurements.

TABLE I

A COMPARISON OF THE TOTAL OXYGEN ABSORBED WITH THE TOTAL PEROXIDE FOUND IN DIBENZYL ETHER

Catalyst	Catalyst, moles/mole of ether	Total O_2 absorbed, cc./mole ether	Total peroxide oxygen, cc./mole ether	Total peroxide in cc. *N*/50 thiosulfate/mole ether
Iodine	0.002	109		..
Benzoquinone	.002	65	...	
Picric acid	.002	30	3.2	29
Water	.010	1309	195.7	1747
Gold	.048	1172	134.7	1203
Silver	.088	1644	499.3	4458
Copper	.149	1745	212.0	1895
Mercury	.047	5233	498.0	4448
Iron	.172	1030	229.0	2044
Dibenzyl ether	...	650	109.0	977

For the titration of the peroxide the oxidized dibenzyl ether is removed from the catalyst, at the end of each experiment, by dissolving it in 30 cc. of pure benzene, the solution filtered and made up to a definite volume, an aliquot part of which is mixed in a special flask with 20 cc. of 5% solution of potassium iodide containing a few drops of freshly prepared starch emulsion and acidified with 5 cc. of glacial acetic acid After fifteen minutes of standing the liberated iodine is titrated against $N/50$ thiosulfate solution, and the flask evacuated and allowed to stand in the dark, with occasional shaking, for ten hours when the final titration is made. Blanks are used at every stage. Later, under the section of oxidized ethers of lower boiling point than dibenzyl, the vacuum treatment is omitted.

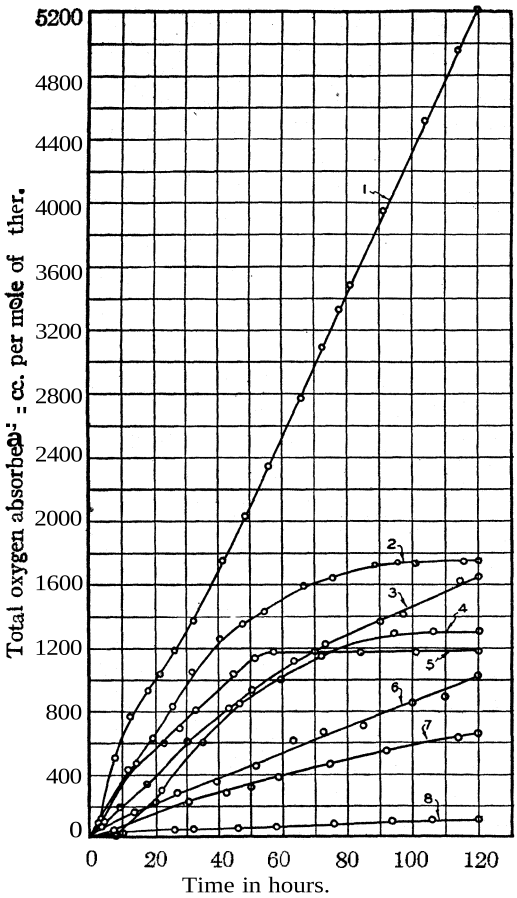

Fig. 2.—Effect of catalysts on the total oxygen absorption of dibenzyl ether. Curve 1, dibenzyl ether + Hg; Curve 2, dibenzyl ether + Cu; Curve 3, dibenzyl ether + Ag; Curve 4, dibenzyl ether + water; Curve 5, dibenzyl ether + Au; Curve 6, dibenzyl ether + Fe; Curve 7, dibenzyl ether alone; Curve 8, dibenzyl ether + I_2.

When a sample of dibenzyl ether in a quartz flask is exposed to ultraviolet light[14] for ten hours at the same temperature but without shaking, the amount of peroxide found corresponds to 1592 cc. of $N/50$ thiosulfate per mole. This is almost twice the peroxide found when the ether is oxidized in the dark for 120 hours.

Among the oxidation products of dibenzyl ether, monoxybenzyl peroxide has been detected by the benzidine reaction, which yielded a deep green color changing quickly to brown. Benzaldehyde was isolated as the derivative of p-nitrophenylhydrazine, m. p. 191°. Benzoic acid was also isolated, m. p. 120.5–121°. An attempt to isolate benzoperacid from the oxidation products by distillation failed because of the high boiling point of the ether, and small amounts of a polymer which is also formed during the oxidation interfered when other methods such as precipitation by an inert solvent were attempted.

It may be remarked here that the catalysts used were of the purest quality obtainable: gold was "Corona" gold purchased from the White Mfg. Co.; silver had been prepared in this Laboratory by the electrolytic precipitation method; iron was in

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[14] For description of the method used, see Section 2.

the powder form prepared by the reduction of iron oxide with hydrogen;, mercury was purified in the usual manner; copper was used in the form of wire 3 to 4 mm. long previously polished and cleaned; iodine was of the pure "reagent" quality; picric acid of the C. P quality, while *p*-benzoquinone was part of a pure sample previously used in other investigations.

Discussion of Results.—From the results shown in Table I and those represented by the curves of Figs. 2 and 3, certain,significant conclusions may be drawn in regard to the auto-oxidation of dibenzyl ether.

Small quantities of inhibitors like iodine, picric acid and benzoquinone show a strong inhibitory action on the oxidation of dibenzyl ether. These substances have also been found to be excellent inhibitors in several auto-oxidation reactions.

Water in small quantities acts as a negative catalyst during the initial stages of the reaction, then as a positive catalyst as the reaction progressed.

Several metals which have been tried in small quantities show a definite acceleration effect. All metals studied were found to have undergone various degrees of oxidation, from a slight tarnish of gold to a complete oxidation of mercury. Silver, which is very resistant to atmospheric oxidation at 40°, was found oxidized to the extent of 2.35%. The results with copper seem to be at variance with those of Hewer,[15] who reports copper to have a retarding influence on the oxidation of ethyl ether.

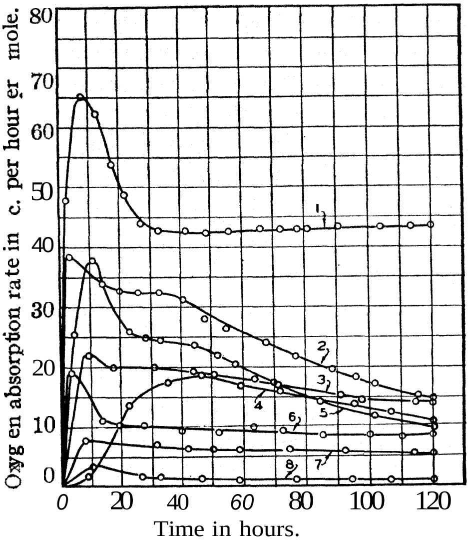

Fig. 3.—Effect of catalysts on oxygen absorption rate of dibenzyl ether. Curve 1, dibenzyl ether + Hg; Curve 2, dibenzyl ether + Cu; Curve 3, dibenzyl ether + Ag; Curve 4, dibenzyl ether + water; Curve 5, dibenzyl ether + Au; Curve 6, dibenzyl ether + Fe; Curve 7, dibenzyl ether alone; Curve 8, dibenzyl ether + I_2.

(2) Auto-Oxidation of Various Ethers under the Influence of Ultraviolet Radiation.—In the foregoing section mention was made of the marked effect of ultraviolet radiation on the auto-oxidation of dibenzyl ether. Similar and more pronounced effects have been observed with several other ethers, the results of which will be presently reported. 1,4-Dioxane, for example, yielded, after eighty hours of continuous exposure to oxygen, an amount of peroxide equivalent only to 6.8 cc. of *N*/50

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[15] Hewer, Lancet, 216, 770 (1929); also quoted in Am. J. Pharm., 101, 840 (1929).

thiosulfate solution per mole, while on exposure to ultraviolet light the amount of peroxide formed for the same period of time was equivalent to 452 cc. of $N/50$ thiosulfate per mole of the ether.

The mechanism of the photochemical oxidation is not very well established at present, but our present results, which should be considered only preliminary, seem to indicate that it follows the same course as that of the oxidation in the dark. This view is particularly strengthened by the fact that the products formed in both reactions are not only identical but are those predicted by our theory. Furthermore, these facts stimulate the conclusion that the primary effect of ultraviolet radiation is to increase the energy content of the molecular valence electrons of the ether oxygen, thereby transforming the whole ether molecule from a relatively inert to a highly activated state. This view is in accordance with the general theory[2a] of auto-oxidation reactions recently proposed by the author. Thereby, the rate with which molecular oxygen combines with ethers to form oxonium peroxides will, presumably, depend not only on the nature of the original ether but also on the statistical average concentration of the activated ether and oxygen molecules present at any moment.

Experimental Procedure and Results

The reactions were carried out in a quartz vessel consisting of a bulb of 1000 cc. capacity and a neck 22 cm. long and 4 cm. in diameter. The neck was provided with an outer condenser jacket through which cold water was allowed to circulate during each reaction. A hollow ground-in pyrex stopper fitted onto the vessel served to connect the latter with a mercury manometer. Dry oxygen was introduced into the apparatus through a small side tube provided with a two-way stopcock and sealed onto one end of the manometer. The reaction vessel was suspended in an air-bath consisting of a rectangular well-insulated tinned iron box 23 X 23 × 36 cm., and ultraviolet light from a standard "Uviarc" lamp was allowed to fall horizontally only upon the bulb of the vessel through a side opening on the box of about the same size as the bulb. In all measurements the lamp was kept at a distance 35 cm. from the bulb. A very efficient fan driven by a high speed motor served to stir the air inside the box, thereby keeping the temperature at about 45 ± 1°.

There seem to be no data available in the literature to show the effect of ultraviolet radiation on the rate of peroxide formation during the oxidation of ethers. It was deemed advisable, therefore, in the present case, to follow the auto-oxidation of ethers by determining the peroxide formed with time of illumination. Although this method fails to account completely for the true rate of auto-oxidation, it affords an excellent semi-quantitative comparison of the tendency with which ethers oxidize.

One hundred cc. of freshly distilled ether, free from peroxide, was added to the quartz vessel after it had been evacuated and filled with pure oxygen. The reaction was then started and the time recorded when the "Uviarc" lamp was turned on. At the end of a definite period of illumination, usually ten hours, the lamp was turned off and the reaction mixture allowed to stand in the dark for one-half hour to acquire the temperature of the room (during this dark period the oxidation of ethers is extremely small, as compared with the photochemical oxidation, and could therefore be entirely neglected without introducing any serious error in the results), then pure oxygen was admitted into the apparatus until the pressure became equal to the atmospheric pressure; the stopper was then removed and by means of a 5-cc. calibrated pipet, samples of 5 cc. were pipetted into an acidified solution of potassium iodide and the iodine liberated titrated against $N/50$ thiosulfate. Best results were obtained when the potassium iodide solution was acidified, just before use, with glacial acetic acid. Blanks were used in every titration. Figure 4 shows the total amount of peroxide found in each of the nine ethers tried expressed in *cc.* of $N/50$ thiosulfate consumed per mole of each ether plotted against time of irradiation. Duplicate runs made with some of these ethers were found to check within 4 to 6%. In addition to these ethers, phenetole, anisole, *p*- and o-methyl cresol and diphenyl ether developed after forty hours of irradiation the following amounts of peroxide expressed in cc. of thiosulfate per mole of each ether: 110.5, 59, 140.4, 115 and 15 cc., respectively. No attempt was made to isolate any of the oxidation products from the aromatic ethers.

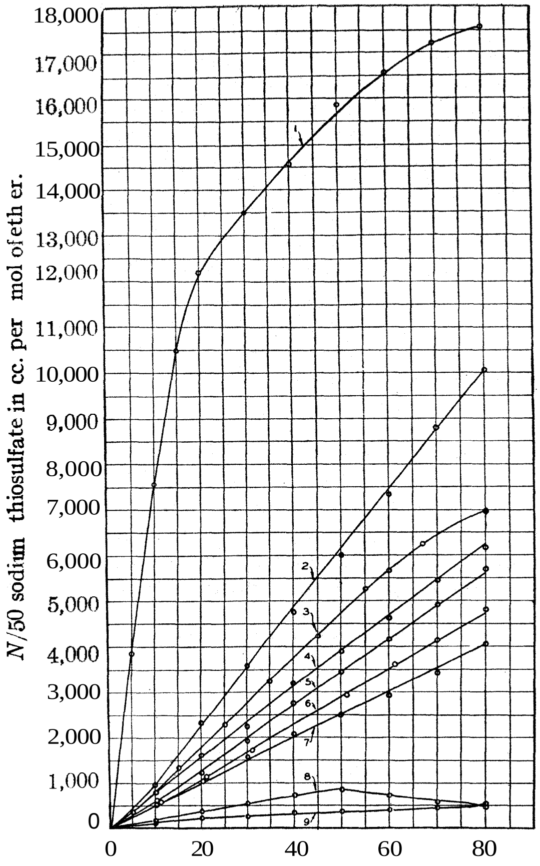

Fig. 4.—Effect of ultraviolet radiation on the oxidation of ethers: Curve 1, *tert.*-butyl benzyl; Curve 2, *sec.*-butyl ethyl; Curve 3, *tert.*-butyl ethyl; Curve 4, *n*-butyl ethyl, Curve 5, isobutyl ethyl; Curve 6, *tert.*-butyl n-propyl; Curve 7, n-dibutyl; Curve 8, 1,4-dioxane; Curve 9, *tert.*-butyl methyl.

Some interesting though only tentative conclusions, at present, seem to emerge from these results. With the majority of ethers studied the total peroxide formed increases, for long periods of time, proportionately with the time of irradiation. The groups to which the ether oxygen is attached exert a decided influence, just as it was anticipated, on the rate with which molecular oxygen adds on to this atom. In other words, the rate with which different ethers autooxidize, under the conditions of our experiments, bears a close relationship to their structure. It would be very interesting, however, to see if these relationships follow when the measurements are made using monochromatic radiation and the quantum yields determined. Such a method of approach is contemplated by the author.

Preparation and Purification of Materials

The following ethers have been prepared and purified in this Laboratory by Dr. George W. Rigby, and details will be found in his Dissertation:[7] *tert.*-butyl ethyl, *tert.*-butyl methyl, *tert.*-butyl n-propyl, n-butyl ethyl, isobutyl ethyl and *sec.*-butyl ethyl. All these ethers have been refractionated over metallic sodium just before use in order to destroy any peroxide that might have developed. The boiling points were found to agree very well with those determined by Dr. Rigby.

n-Dibutyl ether and 1,4-dioxane were the C. P. products purchased from the Eastman Kodak Company. Both of these ethers, but especially the latter, showed the presence of considerable amounts of peroxide and were further purified by fractionating over metallic sodium. It is quite interesting to note that 1,4-dioxane has been variously reported[16] to be indifferent to several oxidizing reagents, and consequently has been highly recommended as a solvent for molecular weight determinations.

Phenetole, anisole and diphenyl ether were also the C. P. products furnished by the Eastman Kodak Company, but were not further purified since they were found to contain only minute traces of peroxides and no aldehydes or phenols.

However, the methyl cresol ethers (Kahlbaum's C. P. quality) contained not only considerable amounts of peroxides, but also aldehydes and organic acids. These were removed and the ethers finally fractionated.

Tert.-butyl benzyl ether was synthesized, for the first time, by us and a brief description of its preparation here will not be irrelevant. Benzyl chloride was mixed with a large excess of sodium *tert.*-butylate and the mixture allowed to stand at room temperature for two months. At the end of this time the mixture was washed with water and the oil which had separated out was dried aver anhydrous sodium sulfate and fractionated, the fraction boiling, with a slight decomposition, at 205.6–208° (corr.) collected and used immediately in our reaction. The density of this ether was found to be d_4^{25} 0.9439. Metallic sodium reacts with it vigorously and therefore cannot be used for its purification. Concentrated hydrochloric acid reacts with this ether, yielding *tert.*-butyl chloride and benzyl chloride. It oxidizes in the dark, yielding monoxy-benzyl peroxide and *tert.*-butyl alcohol. Attempts to separate the peroxide in the pure form were not successful. Both benzaldehyde and benzoic acid have been isolated from its oxidation products.

TABLE II

BOILING POINTS OF ETHERS

Ether	B. p., °C.	Literature
Tert.-butyl methyl	55.3	54-55
Tert.-butyl ethyl	73.1	70
Tert.-butyl n-propyl	97.4	
Tert.-butyl benzyl	205.6–208	..
n-Butyl ethyl	92.3	91.4
n-Butyl n-butyl	142.2–143	140.9
Isobutyl ethyl	81.1	78–80
Sec.-butyl ethyl	81.2	..
1,4-Dioxane	100.9–101.1	101.2–101.4
Methyl o-cresol	170.1–171.6	171.3
Methyl *p*-cresol	175.5–176.0	176.5

No oxidation products of ethers other than the peroxides have been determined quantitatively. Attempts have been made, however, to iso-

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[16] Anschiitz and Broeker, Ber., 59, 2844 (1926); Reid and Hofmann, *Ind.* Eng. Chem., 21, 695 (1929).

late and identify all the important products. Hydrogen peroxide was identified in the oxidation products of all ethers studied by the titanium sulfate test and by Jorissen's vanadic acid reagent.[17] All aliphatic oxidized ethers studied yielded a strong benzidine reaction, which has been ascribed by Woker,[9] Wieland and Wingler[4] and others to the presence of monoxy-alkyl peroxides. The aldehydes were identified by the preparation of their *p*-nitrophenylhydrazones, which were found to have melting points agreeing very well with those recorded in the literature. *Sec.*-butyl ethyl ether yielded in addition to acetaldehyde methyl ethyl ketone.

The hydrazone of glycolic aldehyde isolated from the oxidation products of 1,4-dioxane is actually an osazone first described by Wohl and Neuberg,[18] m. p. 311°. Dakin and Dudley[19] prepared it from glycolic acid, m. p. 302°, and Curtius[20] from glyoxal, m. p. 308°. Our product was recrystallized several times from hot pyridine into fine red needles, m. p. 308.7°. With this osazone alcoholic potash gives a greenish-blue color, changing to deep blue and slowly to violet and finally to reddish-brown. That the aldehyde formed during the oxidation of 1,4-dioxane was not glyoxal was proved by its failure to reduce ammoniacal silver nitrate solution and its positive reaction with Fehling's reagent.

Tert.-butyl alcohol was isolated as the *tert.*-butyl choride, b. p. 50–51°, from the oxidation products of all *tert.*-butyl ethers. Alcohols formed during the oxidation of the other ethers oxidized further and it was, therefore, impossible to isolate them as such.

Another oxidation product detected in small quantities by the mercuric chloride test in all ethers having either the methyl or ethyl groups is formic acid. This acid was also isolated from the oxidation products of 1,4-dioxane.

Isolation of Some Organic Peroxides.—Four of the oxidized ethers were washed with sodium carbonate solution, dried and the unchanged ether removed by distillation in a vacuum at temperatures varying from 0 to 70°, the receiver being cooled in a mixture of solid carbon dioxide and ether. Portions of the residue were then analyzed for active oxygen by the potassium iodide–thiosulfate method, and for the amount of aldehyde formed on hydrolysis in dilute sulfuric and subsequent distillation of the aldehyde by precipitation with *p*-nitrophenylhydrazine. Three trial determinations by the latter method with known samples of propionaldehyde gave recoveries of the aldehyde of 95.6, 94.3 and 95.2%.

The analytic data obtained are given in Table III. The calculated ratio of aldehyde to peroxide is based on the assumption that the first

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[17] Jorissen, *Ann. chim. anal.*, *8*, 201 (1903).

[18] Wohl and Neuberg, *Ber.*, 33, 3107 (1900).

[19] Dakin and Dudley, *J. Biol. Chem.*, *15*, 137 (1913).

[20] Curtius, *J. prakt. Chem.*, [2] 95, 225 (1917).

formula of each possible pair is considered to be monoxy-alkyl perester [RC(=O)—O—O—CH(OH)R], which on hydrolysis should yield aldehyde in the ratio of 1:1 of peracid, while the second formula representing dioxy-alkyl peroxide [R—CH(OH)—O—O—(OH)CH—R] on hydrolysis should yield aldehyde in the ratio of 2:1 of peroxide.

TABLE III

ANALYTICAL DATA

Ether formula	Possible formula of peroxide	Active oxygen Calcd.	Active oxygen Found	Ratio Aldehyde/Peroxide Calcd.	Ratio Aldehyde/Peroxide Found
tert.-$C_4H_9OC_2H_5$	$C_4H_8O_4$	13.33	13.14	1	0.71
	$C_4H_{10}O_4$	13.11	13.00	2	
tert.-$C_4H_9OC_3H_7$-*n*	$C_6H_{12}O_4$	10.81	11.12	1	0.70
	$C_6H_{14}O_4$	10.66	11.30	2	
n-$C_4H_9OC_4H_9$-*n*	$C_8H_{16}O_4$	9.09	8.88	1	0.72
	$C_8H_{18}O_4$	8.99	8.75	2	
i-$C_4H_9OC_2H_5$	$C_6H_{12}O_4$	10.81	10.58	1	0.68
	$C_6H_{14}O_4$	10.66	10.39	2	

These peroxides are all colorless oils which explode violently when heated directly in a flame and possess an odor resembling that of peracids. In ether solution they fail to give the benzidine or chromic acid reactions, but liberate iodine readily from a solution of potassium iodide and give a strong red color with *p*-amidodimethylaniline hydrochloride.

Inasmuch as the peroxide content differs only slightly in the two types of peroxides shown in the foregoing table, it was thought advisable to synthesize the dioxy-ethyl and dioxy-propyl peroxides and compare their behavior toward different reagents with that of the peroxides isolated from *tert.*-butyl ethyl and *tert.*-butyl n-propyl ethers.

The dioxy-propyl peroxide was prepared by allowing a 2:1 mixture of propionaldehyde and hydrogen peroxide in dry ether to stand at room temperature for twenty-four hours. Thereafter the mixture was treated and analyzed in the same manner employed above with the oxidized ethers. The percentage of active oxygen was found to be 10.10 as against 10.66 calculated for $C_6H_{14}O_4$, while the ratio of aldehyde to peroxide was 1.86:1 as against 2:1 calculated. This peroxide has a very disagreeable odor, fails to liberate iodine from neutral potassium iodide and gives only a very weak test with *p*-amidodimethylaniline hydrochloride. It clearly differs from the peroxide isolated from oxidized *tert.*-butyl n-propyl ether.

The dioxy-ethyl peroxide was also prepared in the same manner and was found to have in ether solution properties similar to dioxy-propyl but different from the peroxide isolated from *tert.*-butyl ethyl ether. An attempt to separate it in the pure form under the same experimental conditions applied to *tert.*-butyl ethyl ether failed to leave any residue for analysis.

It is now quite obvious, from the evidence presented, that the peroxides isolated from the oxidation products of four ethers are different from the monoxy-alkyl and dioxy-alkyl peroxides, and therefore might be considered as peresters of the type described. However, neither the monoxy- nor the dioxy-alkyl peroxides are to be excluded from the oxidation products of ethers.

The author takes this opportunity to express profound appreciation to Professor James F. Norris for his coöperation.

Summary

1. Evidence has been brought forward to show that the dehydrogenation theory of Wieland, as applied by Wieland and Wingler to the auto-oxidation of ethers, is untenable.

2. The oxonium peroxide theory, based on previous views of the author, has been proposed to explain the auto-oxidation of ethers.

3. The rate of oxygen absorption by dibenzyl ether has been determined at 40°, and the effect on this rate of the metals gold, silver, copper, iron and mercury, of water, and of iodine, picric acid and benzoquinone has been studied.

4. Ultraviolet radiation has been shown markedly to accelerate the oxidation of various ethers. The rate of peroxide formation under these conditions has been found to depend largely on the type of groups attached to the oxygen atom of the ether.

5. *Tert.*-butyl benzyl ether has been prepared for the first time.

6. The oxidation products of several of the ethers have been identified, and four peroxides have been isolated and shown to differ in properties from monoxy- and dioxy-alkyl peroxides.

CAMBRIDGE, MASSACHUSETTS

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE PREPARATION OF NITROMETHANE

BY PETER P. PRITZL AND HOMER ADKINS

RECEIVED SEPTEMBER 25, 1930 PUBLISHED JANUARY 12, 1931

The reaction of a metallic nitrite with an alkyl halide produces varying proportions of the nitroparaffin and alkyl nitrite depending upon the particular metal, alkyl group and halogen involved. In continuing a study of this reaction,' the reaction of the salts of halogenated acids with sodium nitrite was investigated. It was found by Bolin in this Laboratory that methyl nitrite was not formed in detectable quantities by the reaction of sodium chloroacetate with sodium nitrite nor ethyl nitrite from sodium a-chloropropropionate. These observations led to attempts to determine what reactions reduced the yield of nitromethane to 35–38% of the theoretical in the standard method for the preparation of nitromethane.[2] Experiments were, therefore, made to ascertain to what extent the low yield of nitromethane was due (1) to mechanical losses, (2) to hydrolysis of chloroacetic acid, (3) to reduction of nitromethane by glycolic acid formed by this hydrolysis, (4) to unreacted sodium nitrite, and (5) to the condensation of nitromethane in the presence of alkali.

For the purposes of comparison the following standard procedure slightly modified from that of Whitmore and Whitmore was adopted. A 40% solution of sodium hydroxide (100–105 ml.) was slowly added with vigorous stirring to a mixture of 100 g. of chloroacetic acid and 100 g. of finely crushed ice until the mixture was just alkaline to phenolphthalein, the temperature being kept below 10". Seventy-three grams of sodium nitrite in 100 ml. of water was added and the mixture slowly heated during twenty-five to thirty minutes to 108–110°. Distillation of nitromethane began when the solution was at a temperature of about 87°. The nitromethane was separated from the water layer and the latter redistilled three to five times until the last distillation yielded approximately 4 ml. of water and 0.3 ml. of nitromethane. The combined fractions of nitromethane was dried over calcium chloride for twelve hours, poured off and distilled, the fraction at 98–101° being saved and weighed as nitromethane. Three successive trials of this method gave yields of 27.5, 26.6 and 26.7 g., the average being 41.6% of the theoretical.

The mechanical loss of nitromethane during the preparation was found to be from 4.9 to 5.1 g. or about 9.0%. This was determined by placing known weights (51 to 64 g.) of the compound in 200 ml. of water and recovering the nitromethane by distillation as in the standard procedure.

The percentage of hydrolysis of sodium chloroacetate under approximately the conditions to which it was subjected during its reaction with sodium nitrite was found to be 14.9%. In this determination 9.5 g. of chloroacetic acid was neutralized as in the standard procedure, and 8.4 g. of sodium bicarbonate and 10 ml. of water added. The mixture was then subjected for a time interval and at temperatures which had previously been determined to be approximately those that occurred in the actual preparation of

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[1] Reynolds and Adkins, THIS JOURNAL, 51, 279 (1929).

[2] Whitmore and Whitmore, "Organic Syntheses," John Wiley and Sons, Inc., New York. 1923, Vol. III, p. 83.

nitromethane. The flask containing the reaction mixture was heated in a water-bath which was raised to a temperature of 90° in eight to nine minutes. The contents of the flask were kept at an average temperature of 90.4' for fifteen minutes, the variation being not more than ±1°. The contents of the flask were then cooled to room temperature in less than one minute. The amount of hydrolysis was calculated from the amount of sodium bicarbonate remaining in the flask. This was determined by the addition of an excess of standard hydrochloric acid, removal of the carbon dioxide by bubbling carbon dioxide-free air through the solution for twenty minutes and then titrating the excess acid. When sodium chloroacetate was subjected to the same conditions except that no sodium bicarbonate was used, the hydrolysis was found to be only 2 3%.

The sodium glycolate formed by hydrolysis apparently has little or no effect upon the preparation except in so far as its formation reduces the amount of sodium chloroacetate available for reaction with sodium nitrite. A reaction mixture to which sodium glycolate had been added gave a yield of 39.6% of nitromethane, which is only 1 or 2% less than the usual yield.

The amount of sodium nitrite remaining in the reaction flask after the distillation of the nitromethane in the standard procedure was found in two analyses to be 18.7 g. and 19.0 g. or an average of 25.8% of the amount originally used. This determination was made by utilizing the fact that ammonium nitrite decomposes to give nitrogen and water. Eighty grams of ammonium chloride and 100 ml. of water were added to the flask containing the residue to be analyzed. The flask was then attached to an apparatus so arranged that the mixture could be subjected to distillation and the evolved gases bubbled through sulfuric acid and sodium hydroxide. Nitrogen was liberated when the reaction flask was at a temperature of 108°. The yields of nitromethane in these two experiments were 45.7 and 41.9% of the theoretical amount. In each of the experiments 800 ± 10 ml. (24°, 740 mm.) of nitrogen was also evolved during the preparation and distillation of the nitromethane.

The method of analysis for sodium nitrite used above was shown to be reliable both for the analysis of solutions containing only sodium nitrite and those containing nitrogenous compounds resulting from the reaction of nitromethane in an alkaline solution. For example, when a solution containing 15.24 g. of sodium nitrite in 75 ml. of water was analyzed the volume of nitrogen obtained was 98.5% of the theoretical amount. In another test of the method of analysis, 15.23 g. of sodium nitrite, 55.5 g. of nitromethane and 84 g. of sodium bicarbonate were placed in 250 ml. of water. The nitromethane was distilled out in the usual way, the recovery being 72.1%. The residue thus containing the condensation products from 15.5 g. of nitromethane and 15.23 g. of sodium nitrite was analyzed for the nitrite. There was found 15.20 g. of nitrite or 99.9% of the amount originally placed in the mixture.

The formation of nitromethane from sodium nitrite and sodium chloroacetate is usually assumed to involve the following reactions as given by Whitmore and Whitmore

$$ClCH_2COONa + NaNO_2 = NO_2CH_2COONa + NaCl \qquad (I)$$

$$NO_2CH_2COONa + H_2O = CH_3NO_2 + NaHCO_3 \qquad (II)$$

These reactions do not explain the vigorous evolution of carbon dioxide that occurs during the preparation nor the highly colored products present during the reaction, nor the nitrogenous tar-like residue. According to Dunstan, Dyrnond and Goulding[3] nitromethane reacts in the presence of

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[3] Dunstan and Dymond, *J. Chem. Soc.*, 59, 430 (1891); Dunstan and Goulding, *ibid.*, 77, 1262 (1900).

sodium bicarbonate to form methazonic acid, water and carbon dioxide, e. g.

$$2CH_3NO_2 + NaHCO_3 \longrightarrow HON{=}CHCH{=}N(O)ONa + CO_2 + 2H_2O \quad \text{(III)}$$

It seems almost certain that this reaction occurs during the preparation of nitromethane, for the conditions are almost identical with those under which methazonic acid has been prepared. The dry residue was found to explode on heating, which is in accord with the observations of Dunstan and Goulding.

A group of experiments was made to ascertain the extent to which nitromethane reacts in the presence of sodium bicarbonate. The weights of sodium bicarbonate (89 g.) and nitromethane (64.6 g.) which would be formed in the preparation according to Reaction II were placed in 260 ml. of water and distilled as in the actual preparation. An exothermic reaction began at 70°, nitromethane distilled over, and carbon dioxide was evolved. The solution went through the color changes from cherry-red to black which are characteristic of the reaction mixture in the preparation of nitromethane. The solution was gradually heated during twenty or twenty-five minutes up to 105–108° as in the preparation, and the recovery of nitromethane determined. The loss was in three experiments 21.5, 19.6 and 22.1 g., respectively, or an average loss of 32.6%. In this loss there is included the 9% mechanical loss referred to above, so that 23 to 24% of the nitromethane used underwent condensation, presumably to methazonic acid.

The fate of the sodium nitrite was thus completely accounted for in that about 50% was converted into nitromethane, of which about 8 to 9% was lost in manipulation, 23 to 24% was converted into methazonic acid and its condensation products and 25 to 26% remained in the residue. About 10% of the chloroacetic acid was unaccounted for but this is probably due to the impracticability of determining the extent of hydrolysis under exactly the conditions that exist in the reaction mixture. It is possible that some of it reacts with the condensation products of nitromethane.

Upon the basis of these experiments it seemed possible that the yield of nitromethane could be increased by reducing the alkalinity in the zone of reaction either by incompletely neutralizing the chloroacetic acid or by modifying the method of bringing the reactants together. An increase in the yield to 46% was actually obtained if the sodium nitrite solution was heated to 100–110° before the solution of sodium chloroacetate was added by way of a dropping funnel. In another experiment the same yield of 46% was obtained as by this method except that in this latter case the chloroacetic acid was only half neutralized.

The most effective way of increasing the yield of nitromethane was to use the method of adding the reactants described in the preceding paragraph and to increase the ratio of chloroacetic acid to sodium nitrite so as to insure the reaction of all of the sodium nitrite. When the salt from 100 g. of chloroacetic acid was allowed to react with 36.5 g. of sodium nitrite the yield of nitromethane based on the sodium nitrite was 65% of the theoretical amount. Yields up to 70% of the theoretical were obtained by using an excess of chloroacetic acid.

Summary

The reactions of sodium chloroacetate and sodium nitrite have been studied and it has been ascertained that in using molecular quantities of the reactants approximately 50% of the nitrite is converted into nitromethane, while about 24% of it gives nitromethane which undergoes further condensation to what is presumably the sodium salt of methazonic acid. About 26% of the sodium nitrite does not react, chiefly because 15% or more of the sodium chloroacetate undergoes hydrolysis to sodium glycolate. The formation of nitromethane may be increased to approximately 75% of the theoretical amount if a sufficient excess of sodium chloroacetate is used to insure the complete reaction of the sodium nitrite. The actual yields of nitromethane obtained were about 9% lower than those given above (50 and 75%) because of mechanical losses on the scale of operation used in obtaining them. The weight of nitromethane actually obtained may be increased by about 10% by modifying the standard method so that the sodium chloroacetate is introduced into the nitrite solution after the latter has been heated to the temperature of reaction.

A method is described for the determination of sodium nitrite in the presence of nitrates and methazonic acid and its condensation products.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE RESEARCH LABORATORY IN ORGANOTHERAPEUTICS, ARMOUR AND COMPANY]

GEOGRAPHIC LOCATION AND THE IODINE CONTENT OF THE THYROID GLAND

BY F. FENGER, R. H. ANDREW AND J. J. VOLLERTSEN

RECEIVED OCTOBER 6, 1930 PUBLISHED JANUARY 12, 1931

The biochemical literature contains but very limited data regarding seasonal fluctuations in any physiological function. We know that the thyroid gland needs iodine to render its secretion active. The amount of iodine in the gland consequently reveals its potency. Seidell and Fenger[1] have shown that a very marked seasonal variation exists in the percentage of iodine present in the healthy, normal thyroid glands of domestic animals. There is, in general, from two to three times as much iodine present in the glands during the summer and fall months as during the winter and spring seasons. The glands on which these conclusions were based were collected at Chicago and represented principally the middle central states.

As a result of an inquiry from Dr. W. L. Aycock of the Harvard Medical School, it was decided to investigate existing conditions in the northern and southern portions of the United States. Hog glands were selected

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[1] Seidell and Fenger, J. *Biol. Chem.*, 13, 517 (1913), and Bulletin 96, Hygienic Laboratory, U. S. Public Health Service. 1914, p. 67.

because the hog is an omnivorous animal like the human race, and because the size of the hog thyroid remains constant throughout the seasons.

Approximately one pound of hog thyroid glands was collected weekly, with a few exceptions, for a period of one year at West Fargo, N. D., our most northern abattoir, and also at Fort Worth, Texas, our most southern plant. Immediately after dissection, the glands were frozen and shipped to Chicago in this condition. On arrival, the glands were thawed out, carefully freed from extraneous tissue and weighed. The glands were next finely minced and dehydrated in *vacuo* at low temperature (85°F.). The fat was removed by means of petroleum ether and the desiccated fat-free material powdered. On the finished powder we determined the ash, P_2O_5 and iodine. Lack of space permits only the showing of the iodine values.

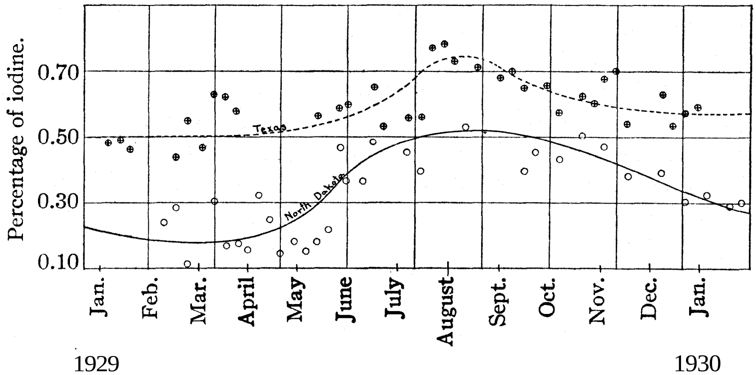

Fig. 1.—Seasonal variation in iodine content of hog thyroid glands from Texas and North Dakota, 1929–30.

Disregarding fluctuations due to the comparatively small number of glands constituting each weekly sample, it will be seen from the chart that both types of glands show seasonal variations in the form of a marked iodine increase during the summer months. The iodine level is higher in the southern than in the northern thyroids but the seasonal fluctuation is more pronounced in the northern glands. The yearly average for the Texas glands is 0.60% iodine with a maximum of 0.78% in August and a minimum of 0.44% in the latter part of February, while that of the North Dakota thyroid is only 0.32% iodine with a top peak at 0.53% in August and a low dip down to 0.13% early in March.

The weight of the fresh glands is not tabulated in this communication. It was found, however, that the fresh southern thyroids were smaller throughout the year and weighed approximately 20% less than the northern glands. The amount of thyroid iodine per unit of body weight is, in spite of this difference, considerably higher in the Texas hogs than in the North Dakota animals. The principal reason for this condition must be sought in the geographic location of the two collection points. The latitude of West Fargo is about 47° north and the winters are quite severe. Fort Worth is situated close to the thirty-third parallel and the winter months are comparatively mild.

Conclusions

Calculated on the desiccated fat-free basis, the yearly average for hog thyroid glands from North Dakota is 0.32% iodine, while that of Texas glands is 0.60% iodine.

The seasonal variation in the iodine content is most pronounced in the northern glands.

The higher iodine level of the Texas glands and the greater seasonal fluctuations of the North Dakota thyroids are attributed to the geographic location of the two states.

CHICAGO. ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRISTOL]

THE ACETYLATION OF ORTHO-HYDROXY ALDEHYDES

BY T. MALKIN AND M. NIERENSTEIN

RECEIVED OCTOBER 10, 1930 PUBLISHED JANUARY 12, 1931

Herzig and Wenzel[1] found that when phloroglucin aldehyde is heated with acetic anhydride and anhydrous sodium acetate, no trace of the corresponding coumarin was produced, and that the condensation product consisted mainly of 2,4,6-triacetoxybenzylidenediacetate (I), which melted at 155–156°. Later, Knoevenagel[2] showed that benzylidenediacetate formation is general to all aromatic aldehydes, being favored by rise of temperature. On the other hand, Pratt and Robinson[3] apparently succeeded in preparing for the first time triacetylphloroglucin aldehyde (II) by the interaction of phloroglucin aldehyde with acetic anhydride and anhydrous potassium carbonate. They found that during the reaction considerable heat was evolved and that the resulting product melted at 151°, a melting point subsequently raised to 156–157° by Robertson and Robinson.[4] The agreement between the melting points found by Herzig and Wenzel and Robertson and Robinson, respectively, for the two substances I and II seemed to us very striking, and since Robinson's triacetylphloroglucin aldehyde is an important starting material in the syntheses of a large number of the anthocyanidins,[5] we thought it desirable to

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[1] Herzig and Wenzel, *Monatsh.*, 24, 864 (1903).

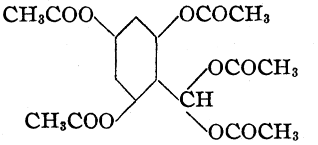
[2] Knoevenagel, *Ann.*, 402, 115 (1913).

[3] Pratt and Robinson, *J. Chem. Soc.*, 127, 1184 (1925).

[4] Robertson and Robinson, *ibid.*, 1713 (1927).

[5] See Pratt and Robinson, *J. Chem. Soc.*, 127, 1182 (1925); Malkin and Robinson, *ibid.*, 127, 1190 (1925); Gatewood and Robinson, *ibid.*, 1959 (1926); Nolan and Robinson *ibid.*, 1968 (1926); Robertson and Robinson, *ibid.*, 1710 (1927); Malkin and Nierenstein, *Ber.*, 61, 791 (1928).

re-investigate this material. Our results leave no doubt whatever that the so-called triacetylphloroglucin aldehyde (II) of Robinson and his co-workers is in fact the penta-acetate (I) of Herzig and Wenzel. This incidentally also offers an explanation for the analytical difficulties commented on by Pratt and Robinson, who found that their product did not give correct values for triacetylphloroglucin aldehyde (II) and assigned to it the empirical formula $C_{13}H_{12}O_7 + {}^1/_2H_2O$.[6]



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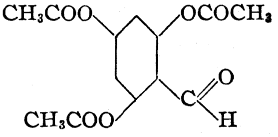

II

In the present communication, a method for the preparation of triacetylphloroglucin aldehyde (II) is described, and this method has also been extended to the preparation of diacetyl-β-resorcylic aldehyde and acetylsalicylic aldehyde. All these aldehydes are smoothly acetylated in ethereal solution with acetic anhydride and anhydrous potassium carbonate in which manner all rise of temperature is controlled. That evolution of heat should be avoided is evident from the fact that if salicylic aldehyde is warmed for a few minutes with acetic anhydride and anhydrous potassium carbonate, 2-acetoxybenzylidenediacetate only is obtained. Cooling in ice does not, however, sufficiently retard the formation of benzylidenediacetate and leads, for example, in the case of phloroglucin aldehyde, to a quantitative yield of the penta-acetate (I) and not the triacetate (II).

The ease with which the formation of benzylidenediacetate takes place clearly accounts in our opinion for the low yields which are obtained when coumarin is prepared by the Perkin synthesis,[7] a fact well known to industry.[8]

The failure of Herzig and Wenzel to obtain 5,7-dihydroxycoumarin by the Perkin reaction is thus in harmony with the facile benzylidenediacetate formation of phloroglucin aldehyde, although Gattermann[9] states that this coumarin is formed by heating phloroglucin aldehyde, anhydrous sodium acetate and acetic anhydride in a sealed tube for five hours at 160–175°. Gattermann, however, draws attention to the fact that the deacetylated product shows no fluorescence in concentrated sulfuric acid, the character-

[6] The analytical data of Pratt and Robinson refer to the product melting at 151°, which was obviously impure penta-acetate (I). No analyses are recorded by Robertson and Robinson for their pure product (m. p. 156–157°).

[7] According to Simonis, "Die Cumarine," Stuttgart, 1916, p. 59, the yield of 37.5% recorded by Gnehm, *Ber.*, 14, 262 (1881), is the highest yield so far given in the literature for coumarin.

[8] See May, ***Perfumery Essential Oil Record,*** 16, *47* (1925).

[9] Gattermann, Ann., 357, 345 (1907).

istic property of 7-hydroxycoumarins. Gattermann's synthesis, therefore, still requires confirmation.

The application of the true o-acetoxy aldehydes in the syntheses of flavylium compounds is in progress, and is reserved for subsequent publications.

Experimental

Phloroglucin aldehyde and β-resorcylic aldehyde were prepared by Adams and Levinc's modification of the Gattermann reaction[10] and only those who have worked with the original Gattermann method can appreciate the advance for which Adams' modification stands. In our experience, however, the comparatively large excess of zinc cyanide as used by Adams and Levine is unnecessary and cleaner products are obtained when only a very slight excess over the theoretical is employed.

Acetyl-salicylic Aldehyde.—To a solution of 10 g. of salicylic aldehyde in 50 cc. of dry ether are added 15 g. of anhydrous potassium carbonate and 15 cc. of acetic anhydride, and the reaction mixture vigorously shaken for thirty minutes. The solution is then filtered on the pump and the residual solid washed several times with dry ether The residue left on evaporation of the ether is treated with water and the solid collected, The product crystallizes from ligroin (b. p. 60–80°) in needles which melt at 38°, in agreement with the melting point given in the literature.

2-Acetoxybenzylidenediacetate.—Ten grams of salicylic aldehyde dissolved in 30 cc. of acetic anhydride is warmed for a few minutes with 10 g. of anhydrous potassium carbonate. The oil formed on pouring into water and standing for some time is separated from the aqueous layer and dissolved in a little alcohol. On standing, thick prisms separate which on crystallization from alcohol melt at 107°. This product is identical with the "2-hydroxybenzylidenediacetate"(m p. 101°) of Perkin,[11] as already pointed out by Barbier[12] and Knoevenagel,[13] who give its melting point as 104–105" and 103°, respectively.

Diacetyl-β-resorcylic Aldehyde.—Three grams of β-resorcylic aldehyde, dissolved in 100 cc. of dry ether, was reacted on with 6 g. of anhydrous potassium carbonate and 10 cc. of acetic anhydride in the manner already described for the preparation of acetylsalicylic aldehyde. The crude product (3.5 g.) separated from absolute alcohol in colorless needles which melted at 69'. The alcoholic solution gives no coloration with ferric chloride.

Anal. Subs., 4.580, 5.101, 4.891 mg.: CO_2, 9.960, 11.150, 10.660 mg.; H_2O, 1.81, 2.12, 1.96 mg. Calcd. for $C_{11}H_{10}O_5$: C, 59.46; H, 4.50 Found: C, 59.31, 59.63. 59.45; H, 4.42, 4.65, 4.48.

Triacetylphloroglucin Aldehyde (II).—For the preparation of phloroglucin aldehyde in small quantities, the following slight modification of the original method of Adams and Levine was found to give excellent results. Into a solution of 2 g. of anhydrous phloroglucin in 25 cc. of dry ether containing, 1.2 g. of zinc cyanide, a good stream of dry hydrogen chloride is passed until the oil formed solidifies. After standing for two to three hours, the solid is collected, washed with ether, and the imide salt dissolved in 40 cc. of water and hydrolyzed on a water-bath. The solid (2 g.) obtained on cooling is collected and dissolved in ether, filtered from traces of a red-colored byproduct, and the ether evaporated. Phloroglucin aldehyde thus obtained crystallizes

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[10] Adams and Levine, THIS JOURNAL, 45,2373 (1923).

[11] Perkin, Ann., 146, 371 (1868).

[12] Barbier, *Compt.* rend., 90, 37 (1881).

[13] Knoevenagel, Ann., 402, 124 (1914).

in long cream-colored needles from water containing a trace of sulfur dioxide. As already recorded by Gattermann, the product has no definite melting point.

In the acetylation, 2.3 g. of phoroglucin aldehyde in 100 cc. of dry ether containing 7.5 g. of anhydrous potassium carbonate and 15 cc. of acetic anhydride are worked up in the manner already described. The crude solid (3 g.) crystallizes from alcohol in thick colorless prisms which melt at 101°. The alcoholic solution gives no coloration with ferric chloride.

Anal. Subs., 5.100, 4.869 mg.: CO_2, 10.420, 9.930 mg.; H_2O, 1.98, 1.85 mg. Subs., 5.333, 5.930 mg.: 5.68, 6.37 cc. of $N/100$ NaOH. Calcd. for $C_{13}H_{12}O_7$: C, 55.71, H, 4.29; CH_3CO, 46.07. Found: C, 55.74, 55.64; H, 4.34, 4.25; CH_3CO, 45.82, 46.21.

The 2,4,6-triacetoxybenzylidenediacetate (I), obtained by the method of Pratt and Robinson, melted at 157".

Anal. Subs., 4.979, 5.075 mg.: CO_2, 9.730, 9.930 mg.; H_2O, 2.06, 2.09 mg. Subs., 6.769, 6.181 mg.: 8.57, 7.81 cc. $N/100$ NaOH. Calcd. for $C_{13}H_{12}O_7$ (triacetylphloroglucin aldehyde): C, 55.71; H, 4.29; CH_3CO, 46.07. Calcd. for $C_{17}H_{18}O_{10}$ (2,4,6-triacetoxybenzylidenediacetate): C, 53.39; H, 4.71; CH_3CO, 56.27. Found: C, 53.30, 53.36; H, 4.63, 4.61; CH_3CO, 54.47, 54.36.

For the micro-acetyl estimations we are indebted to Dr. Arnulf Soltys and to Dr. M. Zacherl, which were carried out by them in Professor Pregl's laboratory, according to the Pregl–Soltys method.''

Summary

A general method for the acetylation of o-hydroxy-aldehydes is described. The acetylation is carried out with acetic anhydride and anhydrous potassium carbonate in the presence of ether, in which manner benzylidenediacetate formation is avoided.

BRISTOL, ENGLAND

[CONTRIBUTION FROM THE BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH, INC., YONKERS, NEW YORK]

A METHOD FOR THE DETERMINATION OF PEROXIDASE ACTIVITY[1]

BY JOHN D. GUTHRIE

RECEIVED OCTOBER 14, 1930 PUBLISHED JANUARY 12, 1931

A mixture of α-naphthol and *p*-phenylenediamine has frequently been used for both the qualitative and quantitative estimation of oxidase activity.[2] This depends on the oxidation of the reagent by atmospheric oxygen to form an indophenol, oxidase acting as the catalyst. In the estimation of peroxidase, hydrogen peroxide takes the place of oxygen in the reaction. The α-naphthol-*p*-phenylenediamine mixture has, however, usually been regarded as too sensitive for peroxidase, and other compounds

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[14] Pregl, "Die Quantitative Organische Mikroanalyse," Berlin, Dritte Auflage, 1930, p. 216.

[1] Herman Frasch Foundation for Research in Agricultural Chemistry, Paper No. 13.

[2] H. M. Vernon, J. *Physiol.*, 42, 402–432 (1911).

have been used for its estimation, especially pyrogallol.[3] It is true that the α-naphthol–p-phenylenediamine reagent is too sensitive for peroxidase when used near the neutral point, but in more acid solutions the reaction is sufficiently slow to be followed quantitatively. Furthermore, catalase is inactive in acid solutions and its interference is, therefore, avoided.

In a previous paper[4] the α-naphthol–p-phenylenediamine reagent was used in a study of peroxidase in potatoes that had been treated with chemicals that break the rest period. The method used in this work gave relative values, only determinations made at the same time being comparable. The procedure has now been improved so that determinations made at different times may be compared.

Preparation of Substrate.—Prepare a citrate buffer, PH 4.5, by dissolving 21 g. of crystalline citric acid in 170 cc. of N sodium hydroxide and diluting to one liter. To 200 cc. of this add 200 cc. of water, 1 g. of p-phenylenediamine hydrochloride, and 20 cc. of 4% α-naphthol in 50% alcohol. Filter the solution.

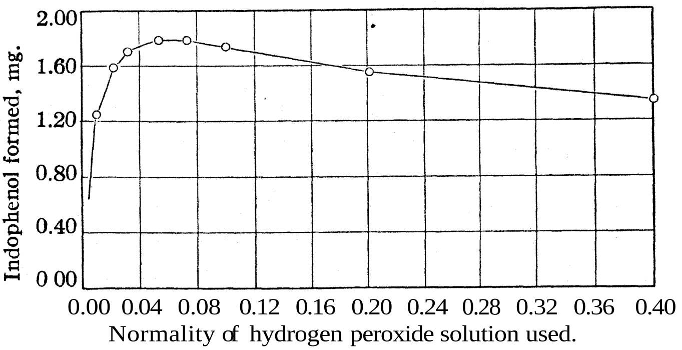

Fig. 1.—Showing the effect of using various hydrogen peroxide concentrations for the determination of peroxidase. Potato juice, 0.5 cc., was used in each determination.

The Method.—Place 25-cc. portions of the freshly prepared substrate in unlipped centrifuge tubes of about 80-cc. capacity. Place in a water-bath at 25° and allow to attain the temperature of the bath. Add 0.5 to 2.0 cc. of the juice or extract containing the enzyme, the amount depending on the peroxidase content. If the extract is very high in peroxidase, it will be necessary to make a known dilution before drawing the sample. Start the reaction by adding 5 cc. of $N/20$ hydrogen peroxide. When ten minutes have elapsed, stop the reaction by adding 5 cc. of 0.1% aqueous solution of potassium cyanide.

Remove from the bath and add 25 cc. of toluene. Stopper with a well fitting cork, shake vigorously and centrifuge. Pour off the clear layer of toluene, which now contains the indophenol, and compare it colorimetrically with the standard. It is usually desirable to run blank determinations on the reagents.

The Standard.—Prepare indophenol by adding 100 cc. of 2 N hydrogen peroxide and 2 cc. of 10% aqueous solution of $FeCl_3 \cdot 6H_2O$ to 800 cc. of the substrate. Allow to

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[3] R. Willstatter and A. Stoll, *Ann.*, **416**, 21–64 (1918).

[4] F. E. Denny, L. P. Miller and J. D. Guthrie, *Am. J. Botany*, 17, 483–509 (1930).

stand overnight. Filter off the precipitated indophenol and purify it by crystallization from a 1:1 mixture of absolute alcohol and toluene.

To make the standard, dissolve 50 mg. of this preparation in 50 cc. of a warm 1:1 mixture of absolute alcohol and toluene. Add toluene to make the total volume one liter. The standard keeps well.

A solution of iodine in chloroform, 2 g. per liter, is also a satisfactory standard. When set at 20 mm. in the colorimeter, it is equivalent to a solution of 75 mg. of the indophenol per liter.

Effect of Hydrogen Peroxide Concentration.-Since Willstätter and Stoll[3] have shown that high concentrations of hydrogen peroxide are harmful to peroxidase, determinations were made using hydrogen peroxide solutions of various normalities. These solutions were standardized with potassium permanganate. The results are shown in Fig. 1. The optimum amount of hydrogen peroxide to use is found to be 5 cc. of $N/20$ solution.

Effect of Concentration of **Enzyme.**—The effect of using various amounts of potato juice is shown in Fig. *2*. The enzyme activity is linear with the concentration of enzyme up to an activity of about *4.0*. It is, therefore, recommended that extracts giving higher values be diluted before drawing the sample.

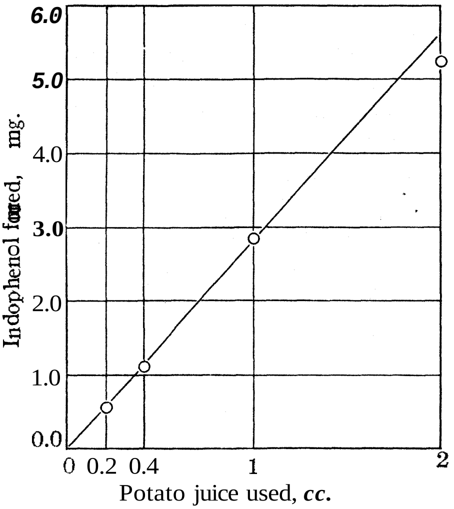


Fig. 2.—Showing the effect of various concentrations of peroxidase, obtained by the use of different volumes of potato juice.

Accuracy of Method.—Potato juice was diluted one-quarter and determinations were made using 2 cc. of the diluted juice. The average indophenol value was 1.48 mg. with an average error of ±0.03 mg.

Summary

A method for estimating peroxidase activity, based on the formation of indophenol from a mixture of *p*-phenylenediamine and a-naphthol in a citrate buffer of PH 4.5, is described.

YONKERS, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

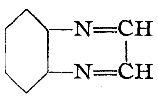
THE RELATION OF QUINOXALINE TO THE AMMONIA SYSTEM

BY F. W. BERGSTROM AND R. A. OGG, JR.

RECEIVED OCTOBER 23, 1930 PUBLISHED JANUARY 12, 1931

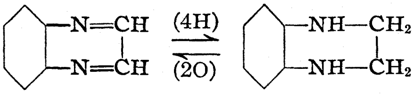
In a recent article[1] the structure of quinoline was discussed from the standpoint of the ammonia system of compounds of Franklin and co-workers, and it was there pointed out that this compound contains the ammono aldehyde grouping —CH=N—, and so should be expected to display properties analogous to those of aldehydes of the water system. In the present work it is desired to apply similar reasoning to the structure of another heterocyclic compound, quinoxaline, and to present experimental confirmation.

From the conventional formula for quinoxaline, A, it is seen that two adjacent ammono aldehyde groups are present in the molecule, and hence it is to be regarded formally as an ammono 1,2-dialdehyde, or ammonoglyoxal.[2] Therefore the properties of quinoxaline, in so far as they involve the heterocyclic ring, should be those of an ammono glyoxal. Some previously known reactions are in accord with this analogy. Thus quinoxaline is synthesized by the action of o-phenylenediamine on glyoxal,[3] a reaction which may be regarded as the ammonolysis of glyoxal by a substituted ammonia, the product being a substituted ammono glyoxal.



A

On reduction quinoxaline behaves as an ammono dialdehyde, yielding the corresponding ammono diprimary alcohol, 1,2,3,4-tetrahydroquinoxaline, which may be oxidized back to quinoxaline.[4]



Several new reactions of quinoxaline have been carried out, the results of which in the main substantiate still further the analogy between this compound and glyoxal.

Quinoxaline and Bisulfites.—Glyoxal behaves as a typical dialdehyde in uniting with two equivalents of acid sulfites. Similarly, quinoxaline has been found to add very readily two equivalents of sodium bisulfite, the solid addition product being easily decomposed by bases with regeneration of quinoxaline.

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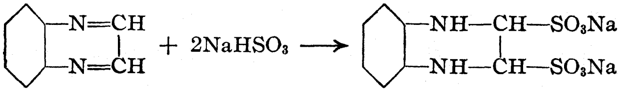
[1] Bergstrom and McAllister, THIS JOURNAL, 52, 2845 (1930).

[2] More correctly, it is to be regarded as an ammono dialdehyde diacetal, since the third valences of the nitrogen atoms are united to an o-phenylene group.

[3] Hinsberg, Ann., 237, 327 (1887).

[4] Merz and Ris, Ber., 20, 1191 (1887). See also Meisenheimer and Wieger, *J. prakt. Chem.*, [2] 102, 45-62 (1921).



Quinoxaline.—This was prepared by the method of Hinsberg[3] from glyoxal sodium bisulfite and o-phenylenediamine. The glyoxal was prepared by the method of Pollak,[5] and the o-phenylenediamine according to the method of Hinsberg and König.[6] The quinoxaline was obtained as a colorless crystalline mass, m. p. 32.0° (corr.),[7] and boiling at 229" (corr.) at 760 mm. It was very soluble in water and organic solvents.

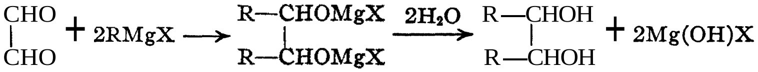
Quinoxaline Sodium **Bisulfite.**—Quinoxaline was added to a nearly saturated aqueous solution of slightly more than two equivalents of sodium bisulfite. Upon the addition of two volumes of ethyl alcohol, a very voluminous precipitate of fine white needles formed. This was filtered off, dissolved in a little water and reprecipitated with alcohol. Samples for analyses were dried in a vacuum over sulfuric acid.

Anal. Subs., 0.4839, 0.1667: Na_2SO_4, 0.2004, 0.0691. Calcd. for $C_8H_8O_6N_2S_2Na_2$: Na, 13.61. Found: Na, 13.41, 13.42.

The product decomposed on heating. By treatment with aqueous solutions of bases, quinoxaline and a neutral sulfite were formed. Acids caused evolution of sulfur dioxide.

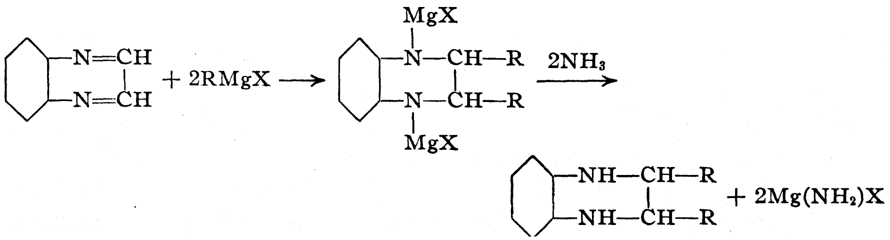
Quinoxaline reacted slowly with sulfurous acid, yielding some sulfuric acid, and an amorphous blue solid which was not further investigated.

Quinoxaline and the Grignard Reagent.—Monomeric glyoxal reacts with two equivalents of a Grignard reagent,[8] the product yielding on hydrolysis the corresponding *dl*-di-secondary alcohol.



$$\begin{matrix}\text{CHO}\\|\\\text{CHO}\end{matrix} + 2\text{RMgX} \longrightarrow \begin{matrix}\text{R—CHOMgX}\\|\\\text{R—CHOMgX}\end{matrix} \xrightarrow{2H_2O} \begin{matrix}\text{R—CHOH}\\|\\\text{R—CHOH}\end{matrix} + 2\text{Mg(OH)X}$$

Quinoxaline has been found to behave in precisely analogous fashion, giving as the final product the corresponding dl-ammono di-secondary alcohol,[8a] i. e., *dl*-1,2,3,4-tetrahydro-2,3-dialkyl-(or aryl)-quinoxaline, in good yield. dl-Tetrahydro-diphenyl- and *dl*-tetrahydro-dimethylquinoxalines were thus prepared, and the method is suggested for the synthesis of other homologs.



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[5] Pollak, Monatsh., 15, 469 (1894).

[6] Hinsberg and König, Ber., 28, 2947 (1895).

[7] Ninsberg gives 27° as the melting point.

[8] Wren and Still, J. Chem. *Soc.*, 103, 1770 (1913).

[8a] Strictly speaking, if the phenylene group is taken into consideration in the naming, we should speak of the di-alkyltetrahydroquinoxalines as mixed ammono di-secondary alcoliol-dihydric phenols.

***dl*-1,2,3,4-Tetrahydro-2,3-diphenylquinoxaline.**—Three grams of quinoxaline in absolute ether was added slowly to ethereal phenylmagnesium bromide (2.2 equivalents) in an atmosphere of nitrogen. The reaction was immediate and vigorous, with precipitation of a semi solid dark brown addition compound. After two hours' standing this was decomposed by careful addition of liquid ammonia (water may also be used). The ammonia was evaporated and the product was extracted with ordinary ether, leaving a residue of ammono basic magnesium bromide. The ether solution was steam distilled, ether first coming over and finally a little diphenyl, the residue being a clear brown gum, vitreous when cold. It was treated with hot concentrated hydrochloric acid and the resulting solid hydrochloride was recrystallized from glacial acetic acid as fine white needles. This was then decomposed with hot aqueous ammonia, regenerating the free base as a colorless vitreous mass, very difficult to crystallize. It was obtained from alcohol as colorless plates, m. p. 106° (corr.). With alcoholic silver nitrate it gave a fine green color and a silver mirror. By acetylation with acetic anhydride and crystallization of the product from alcohol, fine white needles were obtained, m. p. 170° (corr.).

The above properties agree with those of dl-tetrahydro-diphenylquinoxaline, described by Hinsberg and König[9a] and Bennett and Gibson.[9b] A sample of this compound prepared by the method of Hinsberg and Konig proved to be identical with the above product. In particular, the diacetyl derivative from each melted at 170° (corr.), and gave the same mixed melting point, proving their identity: yield of *dl*-tetrahydro-diphenylquinoxaline by the Grignard reaction, 70% of the theoretical.

***dl*-1,2,3,4-Tetrahydro-2,3-dimethylquinoxaline.**—Three grams of quinoxaline in absolute ether was slowly added to ethereal methylmagnesium iodide (2.2 equivalents) in an atmosphere of nitrogen. The addition product settled out rapidly as a dark oil, and after an hour was decomposed with liquid ammonia as above. The product was extracted with ether, which was then evaporated off in a vacuum desiccator, leaving a partially crystalline red residue. This was dissolved in 25 cc. of hot alcohol and added to a solution of 2.8 g. of crystalline oxalic acid in 10 cc. of hot alcohol. After several hours in the cold, the copious crystalline precipitate (oxalate of the base) was filtered off, washed and recrystallized from alcohol. After filtration, the precipitate was decomposed with aqueous ammonia, the free base then being extracted from the solution with benzene. Evaporation of the benzene left a yellowish crystalline mass, which could be crystallized from ligroin or water as fine colorless plates, m. p. 101° (corr.). With aqueous ferric chloride a magnificent blue coloration was produced.

Gibson[10] gives 101° as the melting point of *dl*-1,2,3,4-tetrahydro-2,3-dimethylquinoxaline. A sample of this compound prepared by Gibson's method from 2,3-dimethylquinoxaline proved to be identical with the above product. Each melted sharply at 101° (corr.), as did a mixture of equal quantities, showing their identity. The yield of dl-tetrahydro-dimethylquinoxaline by the Grignard reaction was 50% of the theoretical.

Quinoxaline and Hydrocyanic Acid.—Glyoxal was found by Pollak[6] to react with two equivalents of hydrocyanic acid, yielding two optically isomeric dicyanohydrins, the dinitriles of dl-tartaric and meso-tartaric acid, respectively.

Quinoxaline has been found to behave in similar fashion, adding two equivalents of hydrogen cyanide to give only one ammono dicyanohydrin,

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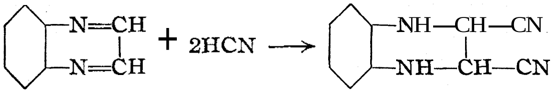
[9] (a) Hinsberg and Konig, *Ber.*, 27, 2181 (1894); (b) Bennett and Gibson, *J. Chem. Soc.*, 123, 1570 (1923).

[10] Gibson, *ibid.*, 342 (1927).

the hitherto unknown 1,2,3,4-tetrahydro-2,3-dicyanoquinoxaline in accordance with the equation

I 

(The optical constitution of this substance was not determined.) This substance was shown to be a secondary diamine, but attempts to saponify it to the corresponding acid were fruitless.

1,2,3,4-Tetrahydrodicyanoquinoxaline.—Ten grams of pure quinoxaline, 7 g. (3.4 equivalents) of anhydrous hydrogen cyanide,[11] and 20 cc. of absolute alcohol were sealed in a bomb tube, which was then heated for two hours at 100" and allowed to stand overnight. The resulting clear yellowish solution was transferred to a beaker and evaporated to dryness in a vacuum desiccator, leaving a crystalline residue. This was extracted twice with carbon tetrachloride (to remove unchanged quinoxaline), and the residue was recrystallized once from water. It was finally purified by precipitation from saturated ether solution by the addition of several volumes of carbon tetrachloride. The crystals so obtained were white prismatic needles, odorless and tasteless, very soluble in alcohol and hot water, moderately soluble in ether, slightly soluble in benzene and cold water and insoluble in carbon tetrachloride. The substance melted at 168.5" (corr.) without appreciable decomposition, but the liquid decomposed above 200°.

Anal. Subs., 0.1416, 0.1455: CO_2, 0.3388, 0.3480; H_2O, 0.0574, 0.0603. Subs. 0.1023, 0.1060: 0.09537 *N* HCl (Kjeldahl), 23.16, 24.00 cc. Calcd. for $C_{10}H_8N_4$: C, 65.19; H, 4.39; N, 30.42. Found: C, 65.25, 65.22; H, 4.54, 4.64; N, 30.25, 30.25.

The yield was about 30%, irrespective of the time of heating. Apparently an equilibrium between quinoxaline, hydrogen cyanide and the addition compound was reached.

The compound did not dissolve in dilute acids and bases. A water solution yielded with nitrous acid an immediate yellow precipitate which gave the Liebermann reaction. The diacetyl derivative was prepared by heating with excess acetic anhydride at 100°. The remaining anhydride was decomposed with alcohol, and the ethyl acetate was removed by evaporation. The gummy residue was dissolved in alcohol and reprecipitated with water. Several repetitions of this process gave colorless prisms, m. p. 93.5" (corr.), very soluble in alcohol, but insoluble in water.

Anal. Subs., 0.0927, 0.0618: 0.09537 N HCl (Kjeldahl), 15.10, 9.95 cc. Calcd. for $C_{14}H_{12}N_4O_2$: N, 20.90. Found: N, 21.76, 21.51.

Attempts to saponify tetrahydro-dicyanoquinoxaline were unsuccessful. Strong bases decomposed it into metal cyanide and quinoxaline, as did a solution of two equivalents of potassium amide in liquid ammonia. Heating with strong hydrochloric acid caused decomposition to a dark tarry mass.

Oxidation of Quinoxaline

Glyoxal is readily oxidized, first to glyoxalic and then to oxalic acid. Quinoxaline was reported by Hinsberg[3] to be resistant to chromic acid, while Gabriel and Sonn[12] found that alkaline permanganate solutions disrupted the benzene ring, yielding a pyrazine-dicarboxylic acid. In the present investigation it was found that by the action of a suitable agent, such as ammonium persulfate, quinoxaline undergoes an oxidation analogous to

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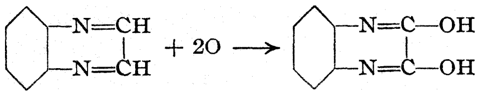
[11] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1927**, Vol. VII, p. 50.

[12] Gabriel and Sonn, *Ber.*, 40, 4850 (1907).

that of glyoxal, yielding an o-phenylene ester of a mixed aquo-ammono oxalic acid, *i. e.*, 2,3-dihydroxyquinoxaline.



2,3-Dihydroxyquinoxaline.—With warm ammoniacal silver nitrate solutions quinoxaline gave a fine silver mirror, but for convenience in isolating the reaction product recourse was had to ammonium persulfate as the oxidizing agent: 1.3 g. of quinoxaline and 15 g. of ammonium persulfate were dissolved in 50 cc. of water, which was then slowly heated to boiling. The solution gradually turned red and deposited a slight brown precipitate. After a few minutes it was cooled and filtered. The filtrate, after evaporation to a small bulk, was nearly neutralized with aqueous ammonia. The resulting precipitate was recrystallized from water, in the form of fine white needles, melting above 300°. This product was shown to be 2,3dihydroxyquinoxaline[13] by converting it into 2,3-dichloroquinoxaline.[14] The substance was heated with excess phosphorus pentachloride at 180° for a few minutes. The melt was decomposed with ice and washed with water. Extraction of the residue with benzene and evaporation of the latter gave a white solid. This was recrystallized from petroleum ether, appearing as fine white needles, m. p. 149.8° (corr.). This substance was 2,3-dichloroquinoxaline, as was shown by the unaltered melting point when it was mixed with a sample of pure 2,3-dichloroquinoxaline, m. p. 149.8° (corr.), prepared by the method of Hinsberg and Pollak.[14] The yield of dihydroxyquinoxaline was about 30% of the theoretical.

Attempts to nitridize quinoxaline in liquid ammonia solution with iodine or ammonium azide were unsuccessful.

Quinoxaline and Potassium Amide.—In the presence of bases glyoxal undergoes an internal Cannizzaro reaction, yielding glycolic acid. Quinoxaline might be expected to undergo an analogous reaction with ammono bases, such as potassium amide, in liquid ammonia, but this was not found to be the case. The reaction of quinoxaline with potassium amide in liquid ammonia apparently follows a complex course, which has not been definitely established. When small amounts (less than one equivalent) of potassium amide were used, the quinoxaline was converted into a viscous, resinous substance. It is suggested that this may be the result of a polymerization of the quinoxaline induced by the ammono base. When two or more equivalents of potassium amide were used, two products were obtained, a dark tarry substance, and a white crystalline precipitate. The latter upon hydrolysis yielded potassium hydroxide and an organic compound which appeared to be fluorubin, described by Hinsberg and Schwantes.[15] Fluorubin is to be regarded as a derivative of ammono oxalic acid, and as a nitridation product of quinoxaline. Inasmuch as no gaseous hydrogen was obtained, equivalent reduction must have taken place, and it is suggested

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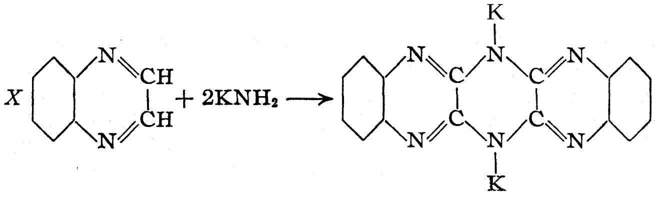
[13] Bladin, *Ber.*, 18, 674 (1885).

[14] Hinsberg and Pollak, *ibid.*, 29, 784 (1896). 2-Hydroxyquinoxaline also yields 2,3-dichloroquinoxaline on fusion with phosphorus pentachloride [Motylewski, ibid., 41, 800 (1908)]. However, 2-hydroxyquinoxaline melts at 269°, whereas the compound obtained melted above 300°.

[15] Himsberg and Schwantes, *ibid.*, 36, 4048 (1903).

that the tarry product may have been a polymerized reduced quinoxaline. It appears at least probable that an external Cannizzaro reaction[16] took place, whose results may be expressed by the following equation, although it is to be emphasized that this is not definitely proved.



+ an equivalent quantity of reduced quinoxaline

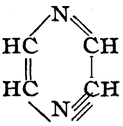
Dipotassium salt of fluorubin

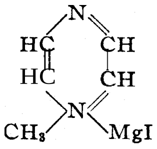
The technique described by Franklin[17] was used in the study of this reaction.

When quinoxaline was treated in liquid ammonia[18] with less than one equivalent of potassium amide, it immediately turned to a dark viscous substance, very soluble in ammonia. No definite compound could be isolated from the mixture. When two or more equivalents of potassium amide were used, the first reaction was the formation of a heavy yellow crystalline precipitate. After a few hours' standing the solution turned deep red and the precipitate became light and voluminous. It was white but very difficult to wash free of the red color. On hydrolysis of the carefully washed salt, a fluorescent green solution and a yellow powder were obtained. The solution proved to contain potassium hydroxide. The yellow powder was washed and dried. It melted above 350° and was insoluble in organic solvents. However, it dissolved in aqueous alkalies to give fluorescent green solutions, and in acids to give intense red fluorescent solutions. These properties agree with those of fluorubin, described by Hinsberg and Schwantes.[15]

Anal. Subs., 0.1234: 0.09537 *N* HCl (Kjeldahl), 26.50 cc. Calcd. for $C_{16}H_{10}N_6$ (fluorubin): N, 29.38. Found: N, 28.69.

The residue from the washings of the salt was a dark tarry substance, from which no pure compounds could be isolated. It is to be noted that mild reduction of quinoxaline leads to complex products.[4]





C

Pyrazine.—It was thought possible that pyraeine, B, which also is formally an ammono glyoxal, might undergo reactions similar to those described for quinoxaline. This, however, was not the case. Pyrazine[19] did not add bisulfites or hydrogen cyanide.[20] With ethereal methyl magnesium iodide, it gave a curdy brown precipitate, probably of the constitution *C*, which yielded no alkyl pyrazine on ammonolysis.

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[16] That is, a reaction similar to the conversion of benzaldehyde to benzyl alcohol and benzoic acid.

[17] Franklin, *J. Phys. Chem.*, **24**, 81 (1920); Strain, This Journal, 49, 1995 (1927).

[18] Quinoxaline is only slightly soluble in liquid ammonia at −33°, but is miscible with it in all proportions at room temperature.

[19] This compound was prepared by the method of Wolff and Marburg, *Ann.*, **363**, 169 (1908).

[20] That is, under the same conditions in which quinoxaline adds sodium acid sulfite or hydrocyanic acid.

Pyrazine was not attacked by iodine in liquid ammonia, although it is to be noted that it can be oxidized in water solution.[21]

Potassium amide in liquid ammonia reacts with pyrazine to form an opaque dirty green solution from which no definite products were isolated.

Discussion

The experimental evidence presented in this article shows the striking analogy between the reactions of glyoxal and those of quinoxaline, substantiating the consideration of the latter as a substituted ammono glyoxal. The usefulness of the ammonia system viewpoint in the study of this and similar heterocyclic compounds is evident. It is intended to show in a later communication how derivatives of quinoxaline may be studied in the same manner.

A point of interest is that in the reactions presented here quinoxaline showed a reactivity more resembling that of an open-chain aldimine than that of a cyclic compound. (Compare the relative inertness of naphthalene, quinoline, etc.) This would seem to indicate definitely the presence of two true double bonds in the heterocyclic ring of quinoxaline.

Summary

1. The behavior of quinoxaline as an ammono glyoxal has been demonstrated by several new reactions. Thus it has been found to add two equivalents of bisulfites, Grignard reagents and hydrogen cyanide, and to undergo oxidation to o-phenylene oxamide. Quinoxaline has been found to react with potassium amide, probably in the sense of the Cannizzaro reaction.

2. **A** new method for the preparation of *dl*-1,2,3,4-tetrahydro-2,3-dialkyl (or diaryl) quinoxalines has been discovered.

3. The following new compounds have been prepared: quinoxaline sodium bisulfite and 1,2,3,4-tetrahydro-2,3-dicyanoquinoxaline.

STANFORD UNIVERSITY, CALIFORNIA

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[21] Stohr, *J. prakt. Chem.*, [2] **51,** *449* **(1895).**

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

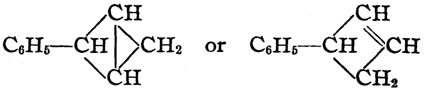
STUDIES OF CONJUGATED SYSTEMS. VI. THE PREPARATION OF THE GEOMETRIC ISOMERS OF METHYLSTYRYLCARBINOL AND OF PHENYLBUTADIENE

BY IRVING E. MUSKAT AND MARGARET HERRMAN

RECEIVED OCTOBER 24, 1930 PUBLISHED JANUARY 12, 1931

In the course of an investigation on the addition reactions of conjugated systems we had occasion to study the preparation and properties of phenylbutadiene. In our early work with this hydrocarbon[1] we encountered considerable difficulty in obtaining consistent results. The yields of phenylbutadiene were at times very good, while again, with the same procedure and under apparently identical conditions, we failed to obtain any of the desired product. A search of the literature revealed that other investigators had encountered similar difficulties.[2] We therefore undertook a thorough study of the preparation of this hydrocarbon with the result that we were able to isolate the geometric isomers of both methylstyrylcarbinol and of phenylbutadiene and have determined the conditions under which to obtain either.

Phenylbutadiene was first prepared by Liebermann[8] by distilling allo-cinnamylidene-acetic acid under diminished pressure. He obtained a very low yield of this hydrocarbon, which distilled at 86° under 11 mm. pressure, and which absorbed two moles of bromine to give a tetrabromide. In a later paper he reported an improved method for the preparation of the same compound by heating cinnamylidene-malonic acid with quinoline.[4] A phenylbutadiene with the same properties was then prepared by Klages,[5] who treated cinnamic aldehyde with methylmagnesium iodide and dehydrated the methylstyrylcarbinol that was formed. Doebner[6] prepared a different phenylbutadiene by the dry distillation of cinnamyl-acrylic acid with barium hydroxide. This phenylbutadiene distilled at 120° under 10 mm. pressure and crystallized to a solid, m. p. 22°. It did not react with bromine, and this led Doebner to assign to it a cyclic structure to indicate its saturated nature.



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[1] Muskat and Huggins, THIS JOURNAL, 51, 2496 (1929); Muskat and Grimsley, *ibid.*, 52,1574 (1930); Muskat and Ludeman, *Ber.*, 62,2284 (1929).

[2] Klages, *ibid.*, 39, 2591 (1906); Straus, *ibid.*, 42, 2882 (1909).

[3] Liebermann, *ibid.*, 33, 2400 (1900).

[4] Liebermann and Riiber, *ibid.*, 35, 2696 (1902).

[5] Klages, *ibid.*, 35,2649 (1902); *ibid.*, 37,2301 (1904).

[6] Doebner, *ibid.*, 35,2129 (1902); *ibid.*, 36, 4318 (1903).

In 1904 Carl von der Heide[7] modified Klages' method for the preparation of phenylhutadiene, which modification has been used more or less satisfactorily ever since. His method is as follows: "To a solution of methylmagnesium bromide (prepared from 30 g. of magnesium) add drop by drop 100 g. of cinnamic aldehyde (instead of the theoretical 160 g.). After standing for twelve hours, decompose under strong cooling with 30% sulfuric acid, wash the ethereal solution with soda and water, dry and distil in a vacuum."

In our earlier work we used essentially the same procedure as that given by Carl von der Heide and obtained, as was stated above, inconsistent results. In order to ascertain the cause of our difficulties we have studied this reaction from every angle, varying every factor that might have some influence on the course of the reaction. The concentration of the Grignard reagent, the temperature at which the reaction occurred, and the rate of addition of the cinnamic aldehyde to the Grignard reagent were varied over a wide range without an appreciable effect on the products of the reaction It was then discovered that the products obtained depended entirely on the decomposition of the intermediate Grignard addition compound and the treatment of the reaction product before distillation.

The intermediate Grignard addition compound was prepared according to the method described by Muskat and Ludeman[1] by treating cinnamic aldehyde with methylmagnesium bromide. If this intermediate Grignard addition compound, to which we shall refer as B, is decomposed with dilute acid and the acid is very carefully washed out of the ethereal solution before distillation, then a new methylstyrylcarbinol is formed which resists dehydration to a marked degree. The structure of this carbinol was proved by ozonization. This *new* methylstyrylcarbinol, although it has nearly the same boiling point as the methylstyrylcarbinol reported by Klages, is decidedly different. *Kluges'* carbinol easily loses water, even on standing for a short time (frequently during distillation if a trace of acid is present), to give the ordinary phenylbutadiene, b. p. 86° under 11 mm. pressure.[2] The *new* carbinol has been kept for many months without the slightest decomposition. Only very strong dehydrating agents will dehydrate it to give, however, a *new* phenylbutadiene, b. p. 76° under 11 mm. pressure. That the two carbinols are true geometric isomers and not structural isomers was definitely established by the reduction of the two carbinols to give the same dihydro derivative, and by the results of an investigation of the chemical properties of the two carbinols, to be presented in a later paper.

If the intermediate B is decomposed with a large excess of 30% sulfuric acid and the acid is carefully washed out of the ethereal solution of the carbinol before distillation, then the new carbinol described above is

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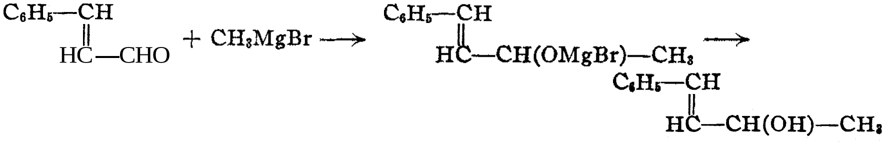
[7] Carl von der Heide, *Ber.*, 37. 2101 (1904).

formed. However, if the acid is not washed out of the carbinol before distillation, a good yield of the ordinary phenylbutadiene is obtained.

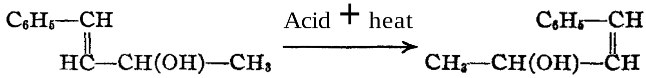
It thus appears that the new carbinol is the normal reaction product of cinnamic aldehyde with methylmagnesium bromide. Inasmuch as cinnamic aldehyde is commonly supposed to have the *trans* configuration,[8] the new carbinol would be represented with the *trans* structure, since the preparation of the carbinol does not involve the double bond which is responsible for the geometric isomerism.



$$\begin{matrix} C_6H_5{-}CH \\ \| \\ HC{-}CHO \end{matrix} + CH_3MgBr \longrightarrow \begin{matrix} C_6H_5{-}CH \\ \| \\ HC{-}CH(OMgBr){-}CH_3 \end{matrix} \longrightarrow \begin{matrix} C_6H_5{-}CH \\ \| \\ HC{-}CH(OH){-}CH_3 \end{matrix}$$

This *trans* structure of the new carbinol was further confirmed by comparing the rates of catalytic hydrogenation of the two carbinols.[9] (It was found that Klages' carbinol[10] was reduced at a faster rate than the new carbinol and according to Paal,[11] who showed that the *cis* isomer is always reduced more rapidly than the *trans* isomer, it would seem that the new carbinol has the *trans* configuration.) This has been confirmed in a similar manner by a study of the relative rates of oxidation of the two carbinols.

If the new *trans* carbinol is treated with dilute acids or even 30% sulfuric acid without heating, then it is neither rearranged to Klages' carbinol nor is it dehydrated to give phenylbutadiene. However, if some of the acid is allowed to remain dissolved in the carbinol, then on distillation it is partially rearranged to Klages' carbinol which, if 30% sulfuric acid has been used, loses water to give ordinary phenylbutadiene. We must then conclude that on warming with acids the *trans* carbinol is rearranged to the *cis* isomer.



$$\begin{matrix} C_6H_5{-}CH \\ \| \\ HC{-}CH(OH){-}CH_3 \end{matrix} \xrightarrow{\text{Acid + heat}} \begin{matrix} C_6H_5{-}CH \\ \| \\ CH_3{-}CH(OH){-}CH \end{matrix}$$

On standing, or in the presence of a dehydrating agent, the *cis* carbinol loses water readily to give Klages' phenylbutadiene, b. p. 86° under 11 mm. pressure. This phenylbutadiene must then have the corresponding *cis* structure.

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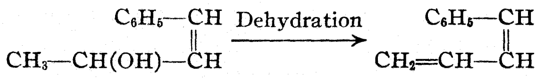
[8] See M. Bourguel, Bull. *soc. chim.*, [4] **45**, 1066 (1929), who has recently prepared the cis isomer of cinnamic aldehyde by the catalytic reduction of the corresponding acetylene derivative. It is planned to prepare a quantity of this new *cis*-cinnamic aldehyde, treat as above with methylmagnesium bromide and determine whether Klages' carbinol is the normal reaction product of this isomer.

[9] This work will be reported in a paper that is to follow.

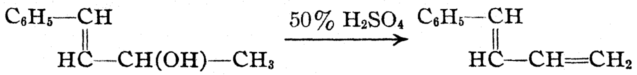
[10] Evidence to be given in the following paper leads us to believe that the carbinol reported by Klages was in reality a mixture of the two geometric isomers. However, we shall use the term "Klages' carbinol" to refer to that carbinol which easily loses water to form the ordinary phenylbutadiene.

[11] Paal, *Ber.*, 60, 1221 (1927); *ibid.*, 63, 766 (1930).



$$\begin{array}{r}C_6H_5\text{—}CH\\ \|\\ CH_3\text{—}CH(OH)\text{—}CH\end{array}\xrightarrow{\text{Dehydration}}\begin{array}{r}C_6H_5\text{—}CH\\ \|\\ CH_2{=}CH\text{—}CH\end{array}$$

If the *trans* carbinol is treated with a very strong dehydrating agent, such as 50% sulfuric acid, a molecule of water is lost to give a new phenylbutadiene, b. p. 76° under 11 mm. pressure. This must therefore have the corresponding *trans* structure.



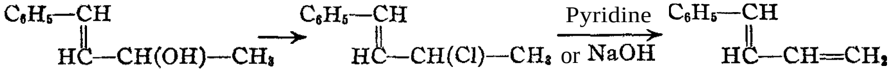
$$\begin{array}{l}C_6H_5\text{—}CH\\ \quad\;\|\\ \quad HC\text{—}CH(OH)\text{—}CH_3\end{array}\xrightarrow{50\%\ H_2SO_4}\begin{array}{l}C_6H_5\text{—}CH\\ \quad\;\|\\ \quad HC\text{—}CH{=}CH_2\end{array}$$

The *cis* and *trans* structures of the two phenylbutadienes as well as the carbinols have been confirmed by the relative rates of catalytic hydrogenation and of oxidation of the two isomers. In each case the isomer to which we have assigned the *cis* structure was hydrogenated more rapidly and oxidized more rapidly than was the *trans* isomer.[9] If the higher boiling *cis* phenylbutadiene is allowed to stand overnight with a trace of acid and then directly distilled, the lower boiling *trans* phenylbutadiene is formed. Obviously the acid rearranges the *cis* phenylbutadiene to the *trans* isomer, while it rearranges the *trans* methylstyrylcarbinol to the cis isomer.

$$\begin{array}{r}C_6H_5\text{—}CH\\ \|\\ CH_2{=}CH\text{—}CH\end{array}\xrightarrow{\text{[redacted]}}\begin{array}{l}C_6H_5\text{—}CH\\ \quad\;\|\\ \quad HC\text{—}CH{=}CH_2\end{array}$$

If methylmagnesium iodide is used to react with cinnamic aldehyde instead of methylmagnesium bromide the conditions are somewhat different. These details are described in the experimental part.

The new *trans* phenylbutadiene can be prepared by treating the tmn: carbinol with dry hydrogen chloride in anhydrous ether solution to form an almost quantitative yield of the chloride. The chloride may now be refluxed for several hours with pyridine or shaken for twenty-four hours with a 5% sodium hydroxide solution at room temperature, either of which removes one mole of hydrogen chloride to give the new *trans* phenylbutadiene in an almost quantitative yield.



$$\begin{array}{l}C_6H_5\text{—}CH\\ \quad\;\|\\ \quad HC\text{—}CH(OH)\text{—}CH_3\end{array}\longrightarrow\begin{array}{l}C_6H_5\text{—}CH\\ \quad\;\|\\ \quad HC\text{—}CH(Cl)\text{—}CH_3\end{array}\xrightarrow[\text{or NaOH}]{\text{Pyridine}}\begin{array}{l}C_6H_5\text{—}CH\\ \quad\;\|\\ \quad HC\text{—}CH{=}CH_2\end{array}$$

In the experimental part the method for the preparation of each of the methylstyrylcarbinols and of the phenylbutadienes will be given in detail.

It is interesting to note that the most striking chemical difference between the two methylstyrylcarbinols lies in the fact that they differ in the ease with which water is lost to give the corresponding phenylbutadiene; yet the geometric difference, the *cis–trans* isomerism, has apparently nothing to do with the tendency to lose water. It is at once clear why cis maleic acid should lose water easily to give an anhydride while the *trans* fumaric should not, but it is difficult to understand why there should be any difference in the ease with which water is lost from the two methylstyrylcarbinols, since the part of the molecule affected supposedly has nothing to do with the geometric isomerism. It may be that the phenyl group in the *cis* position has a loosening influence on the hydrogen atoms of the methyl group. This suggestion finds some support in the fact that the hydroxyl group of the *trans* carbinol seems to be fully as reactive as the hydroxyl group of the *cis* carbinol, and therefore the difference in the ease of eliminating water from the two carbinols must depend on the hydrogen atoms of the methyl group.

Experimental Part[12]

The Preparation of the Intermediate Grignard Addition Compound B.—The intermediate Grignard addition compound was prepared according to the method of Muskat and Ludeman.[1] "Methylmagnesium bromide is prepared in the usual manner from 40 g. of methyl bromide and 10 g. of magnesium. The manipulation is much easier and the loss is much less if the methyl bromide is allowed to pass into the ether suspension of the magnesium turnings as a gas from a cylinder instead of added as a liquid (b. p. 4.5°) through a dropping funnel. Thirty grams of cinnamic aldehyde (free of cinnamic acid and dried over calcium oxide) is allowed to drop in slowly, the reaction flask being immersed in an ice–salt mixture during the process. The theoretical amount of cinnamic aldehyde (53 g.) is not used, for only part of the cinnamic aldehyde combines with the Grignard reagent; the rest polymerizes to a resin. . . . ." In this work we used three times the quantities of the reagents given above, and the addition compound was allowed to stand overnight before decomposition. The Grignard addition compound prepared in this way will be referred to as B.

Decomposition of the Intermediate Grignard Addition Compound B

(a) With Dilute Acids. The Preparation of *Trans* **Methylstyrylcarbinol.**—The intermediate Grignard addition compound B was decomposed with sufficient dilute (about 10%) acid (sulfuric, hydrochloric or acetic acid may be used) to dissolve the magnesium hydroxide. The decomposition was effected by gradually pouring the intermediate B into a large flask containing a mixture of ice and dilute acid. A mechanical stirrer was used to keep the mixture in constant agitation and thus avoid localized heating. The decomposition mixture was extracted with ether, the ethereal solution very carefully washed free from acid, dried over anhydrous sodium sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure, the residual oil, with the exception of a small fraction, distilled over completely at 117° under 4 mm. pressure. Its boiling point was determined at several pressures: 116.5° at 3.5 mm., 117.5° at 5 mm., 123° at 7.5 mm. pressure. It is a stable compound and may be kept for many months without the slightest decomposition. Its refractive index at 31° is 1.5550.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.03; H, 8.16. Found: C, 81.02, 81.03; H, 8.20, 8.21. Calcd. for $C_{10}H_{12}O$: mol. wt., 148.09. Found: mol. wt., 149.1.

The method of preparation and the above analyses indicate that the compound is methylstyrylcarbinol, $C_6H_5—CH=CH—CH(OH)—CH_3$; however, its chemical and physical properties are at variance with those of the methylstyrylcarbinol reported

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[12] The authors wish to express their appreciation to Mr. Charles Marshall for his aid in the preparation of some of these compounds.

by Klages.6 That it really is a methylstyrylcarbinol was proved by subjecting it to ozonization. The carbinol (10 g.) was dissolved in chloroform and a current of ozonized oxygen was bubbled through the solution for several hours. An ozonizer similar to the one described by Harries[13] was used. After the ozonization was complete the chloroform was removed by vaporization under reduced pressure and the residual viscous ozonide was decomposed with water. To insure the complete decomposition of the ozonide it was warmed on the water-bath for a short time. The mixture consisted of aldehydes and acids and was separated into its components by extracting the alkaline solution several times with ether. The ethereal solution was dried and the ether removed by vaporization. A solid (0.9 g.) remained which melted at 120°. It was crystallized once from water and melted at 122°, the melting point of benzoic acid. A mixture with pure benzoic acid also melted at 122°. The water extract gave a positive Uffelman test for lactic acid, the second oxidation fragment of the carbinol.

The ethereal solution of the aldehydes was again washed with alkali and the ether was removed by vaporization. The residue, an oil, was treated with an aqueous solution of semicarbazide hydrochloride in the usual manner. A semicarbazone (8.8 g.) was precipitated after a time. This was removed and dried. It melted at 209°. It was recrystallized several times from alcohol and melted at 214°, the melting point of the semicarbazone of benzaldehyde. When it was mixed with the synthesized product the melting point of the mixture was not lowered. This corresponds to a 90.8% yield of benzaldehyde.

It is of paramount importance for the preparation of this *trans* methylstyrylcarbinol to wash all traces of acids from the ethereal solution of the carbinol before distillation. It is also better to use anhydrous sodium sulfate rather than calcium chloride to dry the ethereal solution, since frequently traces of acid may be introduced by the calcium chloride.

The above preparation was repeated except that the acid was not washed out of the ethereal solution of the carbinol before distillation On distilling the residual oil a mixture of the *trans* carbinol and a small amount of Klages' *cis* carbinol was obtained. The presence of the latter was indicated by the fact that the distillate became cloudy shortly after distillation. The cloudiness is due to the water split from the *cis* carbinol The ready loss of water is a characteristic property of this compound. Frequently during distillation a portion of the *cis* carbinol will decompose to give phenylbutadiene and droplets of water. We must therefore conclude that the *trans* carbinol rearranges to the *cis* carbinol when it is warmed in the presence of acid.

That this rearrangement is due to the warming with acid and not merely to the presence of acid was confirmed in the following manner. The pure *trans* carbinol was shaken with 30% sulfuric acid at room temperature (about 25°) for twelve hours. It was then divided into two portions. The first portion was extracted with ether, the ethereal solution was very carefully washed free from acid, dried over anhydrous sodium sulfate, and the ether was removed by vaporization. The residual oil distilled over completely at 117° under 4 mm. pressure without the slightest indication of the presence of any *cis* carbinol. The second portion was worked up in exactly the same way except that the acid was not all washed out of the carbinol before distillation. During the distillation of the residual oil a great deal of water was split out and a mixture of phenylbutadiene, *cis* carbinol, droplets of water and some *trans* carbinol distilled over. This proves conclusively that it is necessary to warm the *trans* carbinol with acid to cause a rearrangement to take place.

(b) With Water.—The intermediate B was hydrolyzed with water, the hydrolysis product was extracted with ether, the ethereal solution dried over anhydrous sodium

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[13] Houben–Weyl, "Die Methoden der Organischen Chemie," 1924, Vol. III, p. 276.

sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure, the residual oil, with the exception of a very small fraction, distilled at 117° under 4 mm. pressure. It was identical with the *trans* carbinol described above.

The yield of the carbinol is much less and the manipulation more difficult by this method than by the method described above using dilute acids to decompose the intermediate B, since the magnesium hydroxide, which results from the hydrolysis of the intermediate B, frequently forms a stable emulsion with the ethereal solution of the carbinol.

(c) With 30% Sulfuric Acid. The Preparation of Ordinary *Cis* **Phenylbutadiene.**—The intermediate B was decomposed with 30% sulfuric acid exactly as described in (a). The decomposition mixture was extracted with ether, the ethereal solution very carefully washed free from acid, dried over anhydrous sodium sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure the residual oil, with the exception of a small fraction, distilled over at 117° under 4 mm. pressure. It was identical with the *trans* carbinol described in (a).

The above preparation was repeated except that the acid was not washed out of the ethereal solution of the carbinol before distillation. On distilling the residual oil a mixture of the ordinary phenylbutadiene, the *trans* and *cis* carbinols and droplets of water was obtained. A considerable portion of the oil distilled at 204° under 3 mm. pressure, which is the boiling point of the dimer of phenylbutadiene. It was observed that whenever the *cis* phenylbutadiene was formed in the course of such a reaction, polymerization occurred to a marked degree.

In order to obtain a good yield of phenylbutadiene the following procedure was used. The intermediate B was poured into a beaker containing a liter of 30% sulfuric acid and no effort was made to keep the reaction cold. It was allowed to stand in contact with the acid overnight. The decomposition product was then extracted with ether, the ethereal solution washed several times with water and dried over anhydrous sodium sulfate overnight. The ether was then removed by vaporization and the residual oil subjected to distillation under reduced pressure. A 60% yield of phenylbutadiene boiling at 86° under 11 mm. pressure, was obtained. It was identical with the phenylbutadiene reported by Klages. Its refractive index at 28° is 1.5950.

It may be well to emphasize the following points in this method for the preparation of *cis* phenylbutadiene. If the intermediate B is decomposed with 30% sulfuric acid under strong cooling and continuous stirring and all of the acid is washed out of the ethereal solution before distillation, then the *trans* methylstyrylcarbinol is formed. If the intermediate B is decomposed with 30% sulfuric acid and no effort is made to cool the reaction or to keep it agitated to prevent localized heating, then the heat of the reaction in the presence of the acid is sufficient to rearrange the *trans* to the *cis* carbinol. Once rearrangement has taken place then the length of contact with the drying agent becomes of paramount importance. If the acid is washed out of the ethereal solution, and the solution is dried but a short time, the *cis* carbinol is the main product of the reaction. If, however, the acid is not washed out, then some decomposition occurs and phenylbutadiene, *cis* carbinol and water result. If the acid is washed out of the ethereal solution after the above rearrangement and the solution is dried overnight, then *cis* phenylbutadiene is obtained. If the acid is not washed out of the ethereal solution and the solution is dried overnight, then on distillation the *cis* phenylbutadiene may be rearranged into the *trans* phenylbutadiene, as will be shown later in the paper.

(d) With 50% Sulfuric Acid. The Preparation of *Trans* **Phenylbutadiene.**—The intermediate B was decomposed with 50% sulfuric acid in a manner entirely analogous to that described in (a). The residual oil was distilled under diminished pressure. A small amount of oil distilled at 76° under 11 mm. pressure and a dark viscous mass remained in the distilling flask. The oil was analyzed and proved to be a lower-boiling phenylbutadiene. Its refractive index at 28° is 1.5920.

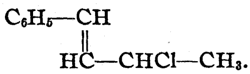
Anal. Calcd. for $C_{10}H_{10}$: C, 92.25; H, 7.75. Found: C, 92.11, 92.21; H, 8.09, 7.90. Calcd. for $C_{10}H_{10}$: mol. wt., 130.08. Found: mol. wt., 132.2.

That it is the *trans* isomer of phenylbutadiene was shown by a study of its chemical reactions, which will be presented in a later paper.

The new *trans* phenylbutadiene can be prepared in a good yield by either of the two following methods.

(1) The *trans* carbinol was dissolved in anhydrous ether and dry hydrogen chloride gas was passed in until no more was absorbed. The flask was immersed in an ice-bath during the reaction. The ethereal solution was washed with dilute alkali to remove the excess acid and then with water until neutral. It was dried over anhydrous sodium sulfate and the ether was removed by vaporization. Upon distillation of the residual oil under diminished pressure, an almost quantitative yield of a light yellow oil distilled at 104° under 6 mm. pressure. It is quite stable and may be kept for several weeks with but little decomposition.

Anal. Calcd. for $C_{10}H_{11}Cl$: Cl, 21.29. Found: Cl, 21.17, 21.21.

The chloride has the structure  $\begin{array}{l} C_6H_5\text{—}CH \\ \quad\ \| \\ HC\text{—}CHCl\text{—}CH_3 \end{array}$. A thorough study of the chemical reactions of this chloride has been made and these will be presented in a later paper.

The chloride was refluxed for several hours with five volumes of pyridine. The reaction mixture was taken up in ether and washed thoroughly with water to remove the pyridine. The ethereal solution was dried over anhydrous sodium sulfate and the ether was removed by vaporization. When subjected to distillation under diminished pressure, the residual oil distilled over almost completely at 76° under 11 mm. pressure, the boiling point of the *trans* phenylbutadiene.

The chloride may be converted into the *trans* phenylbutadiene by shaking for twenty-four hours with approximately twice the theoretical amount of 5% sodium hydroxide. The reaction mixture is extracted with ether, the ether solution washed until neutral, dried over anhydrous sodium sulfate and the ether removed by vaporization. Upon distillation of the residual oil *an* almost quantitative yield of *trans* phenylbutadiene is obtained.

(2) The *trans* phenylbutadiene may be prepared by rearranging the *cis* phenylbutadiene. The rearrangement may be effected by allowing the *cis* phenylbutadiene to stand overnight with a trace of acid. A few pieces of calcium chloride moistened with dilute hydrochloric acid are added to the *cis* phenylbutadiene and, after standing overnight, the compound is distilled under reduced pressure. The lower-boiling *trans* phenylbutadiene distils at 76° under 11 mm. pressure. The yield is quantitative.

The Preparation of the Intermediate Grignard Addition Compound I.—The intermediate Grignard addition compound I is prepared in exactly the same manner as the intermediate Grignard addition compound B, except that methylmagnesium iodide is used in place of methylmagnesium bromide. The intermediate I is much less soluble in ether than is the intermediate B.

Decomposition of the Intermediate Grignard Addition Compound I.—The intermediate I was decomposed with dilute sulfuric acid in a manner entirely analogous to that described above for the corresponding methylmagnesium bromide intermediate B. The decomposition mixture was extracted with ether and the ethereal solution was washed with sulfurous acid to reduce the iodine that was set free. The intermediate

I may be decomposed directly with a saturated solution of sulfurous acid and thus avoid the preliminary treatment with dilute acid. After all of the iodine had been removed the ethereal solution was washed with water until neutral. A large number of washings were required to remove all of the sulfurous acid. The ethereal solution was dried over sodium sulfate and the ether removed by vaporization. When subjected to distillation under reduced pressure, the residual oil distilled over almost completely at 117° under 4 mm. pressure. It was identical with the *trans* carbinol described above.

The Preparation of *Cis* **Methylstyrylcarbinol.**—The above preparation was repeated except that the ethereal solution of the carbinol was washed only twice with water before distillation, thus leaving some of the sulfurous acid in solution. On distilling the residual oil, the cis methylstyrylcarbinol was obtained, b. p. 144° under 21 mm. pressure. It was identified by its characteristic tendency to lose water.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.03; H, 8.16. Found: C, 81.12, 81.10; H, 8.30, 8.27. Calcd. for $C_{11}H_{12}O$: mol. wt., 148.09. Found: mol. wt., 150.0.

This method is the most reliable for the preparation of *cis* methylstyrylcarbinol. Its refractive index at 31° is 1.5536.

If the above method of preparation is repeated and none of the acid is washed out, then on distilling the residual oil a small yield of the trans phenylbutadiene is obtained, and a dark viscous polymer remains in the distilling flask.

Summary

1. The isolation of the geometric isomers of methylstyrylcarbinol have been given and their geometric structures determined.
2. The isolation of a new geometric isomer of phenylbutadiene is given.
3. The geometric structures of the two isomeric phenylbutadienes were determined.
4. Methods for the preparation of each of the geometric isomers of methylstyrylcarbinol and of phenylbutadiene are described.
5. Methods of rearranging the above geometric isomers are given.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES OF CONJUGATED SYSTEMS.
VII. THE CHEMICAL REACTIONS OF THE GEOMETRIC ISOMERS OF METHYLSTYRYLCARBINOL

BY IRVING E. MUSKAT AND MARGARET HERRMAN

RECEIVED OCTOBER 24, 1930 PUBLISHED JANUARY 12, 1931

In the preceding article[1] we gave a detailed description of the methods of preparation of the geometric isomers of methylstyrylcarbinol and of the corresponding phenylbutadienes. The present paper contains the results of an investigation of the chemical reactions of the two geometric isomers of methylstyrylcarbinol.

The reactions studied have been of two general types: *i. e.*, reactions of the hydroxyl group, and reactions involving the double bond. In the

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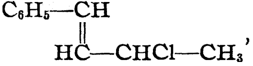
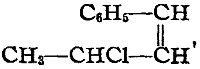
[1] Muskat and Herrman, THIS JOURNAL, 53, 252 (1931).

following pages we shall present, under these two heads, a comparison of the behavior of the two geometric isomers of methylstyrylcarbinol.

I. Reactions of the Hydroxyl Group

Klages[2] reported the preparation of the phenylurethan, m. p. 94°, of his *cis* carbinol. We have been unable to duplicate his results with the pure *cis* carbinol, although the *trans* carbinol does give a quantitative yield of a phenylurethan of the same melting point and apparently of the same crystalline structure. Therefore it seems evident to us that the results reported by Klages were obtained on a mixture of the two carbinols rather than from the pure compound. It must be remembered that Klages was not aware of the existence of the *trans* isomer of methylstyrylcarbinol

Burton[3] also reported a phenylurethan, m. p. 94°, from methylstyrylcarbinol prepared by Klages' method. In addition Burton reported the preparation from his carbinol of an acetate which is identical with the acetate we prepared from the *trans* carbinol. The *cis* carbinol is dehydrated under the conditions used to prepare the acetate of the *trans* carbinol. This is confirmatory evidence for our previous statement that the urethan reported by Klages resulted from the *trans* carbinol. It is significant that the previous investigators of methylstyrylcarbinol, who were unaware of the existence of geometric isomers of methylstyrylcarbinol, frequently purified their product in such a manner as to remove any *cis* carbinol present in the mixture they first obtained.

The *trans* carbinol, when treated with dry hydrogen chloride in anhydrous ether solution, reacts to form a *trans* chloride,  $\begin{array}{l} \quad C_6H_5{-}CH \\ \quad\quad\ \| \\ \quad HC{-}CHCl{-}CH_3 \end{array}$, b. p. 104° under 6 mm. pressure. Under the same conditions the *cis* carbinol reacts with hydrogen chloride to form a *cis* chloride,  $\begin{array}{r} C_6H_5{-}CH \\ \| \\ CH_3{-}CHCl{-}CH \end{array}$, b. p. 108° under 6 mm. pressure. Klages[2] has reported the preparation in a similar manner of *a* chloride from his methylstyrylcarbinol, but he stated that the chloride was so unstable that he was able neither to distil it nor to obtain even an approximate analysis. We have found that if all of the excess hydrogen chloride is not washed out of the ethereal solution of the chloride before distillation, then the chloride decomposes during distillation. However, if the acid is carefully washed out, then the chlorides of either of the carbinols may be distilled without the slightest decomposition. It is interesting to note that hydrogen chloride did not add to the double bond of either of the carbinols. The chloride obtained from the *cis* carbinol was found to be identical with the chloride obtained from the addition of hydrogen chloride to the *cis* phenylbutadiene.[4]

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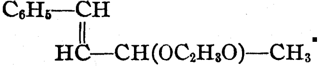
[2] Klages, *Ber.*, 35, 2649 (1902).

[3] Burton, *J. Chem. Soc.*, 132, 455 (1929).

[4] To be reported in a later paper.

The *trans* chloride was refluxed with a 10% solution of sodium acetate for several hours. A product was obtained which distilled at 118° under 4 mm. pressure, and which was identified as the acetate,



$$\begin{array}{l}C_6H_5\text{—}CH\\ \quad \| \\ \quad HC\text{—}CH(OC_2H_3O)\text{—}CH_3\end{array}$$

. This acetate is identical with the acetate prepared directly from the *trans* carbinol as given above. A condensation product of the *trans* carbinol was also obtained. This condensation product will be referred to later in the paper.

When the *trans* chloride was refluxed with silver oxide until all of the chloride had reacted, a small amount of the *trans* phenylbutadiene, b. p. 76° under 11 mm. pressure, was obtained with a preponderance of the polymer of this phenylbutadiene, b. p. 194° under 3 mm. pressure.

The *trans* chloride was refluxed with about five times its volume of pyridine for several hours. An almost quantitative yield of the *trans* phenylbutadiene, b. p. 76° under 11 mm. pressure, was obtained. Under the same conditions the *cis* chloride gave about 40% of the *cis* phenyl butadiene, b. p. 86° under 11 mm. pressure, the rest being polymerized to the dimer.

The *trans* chloride was shaken with two moles of 5% sodium hydroxide for approximately twenty-four hours. An almost quantitative yield of the *trans* phenylbutadiene was obtained. Under the same conditions the *cis* chloride gave a very small amount of the cis phenylbutadiene, the rest being polymerized to the dimer.

The reactions of the carbinols with varied concentrations of sulfuric acid to cause rearrangement or dehydration have been amply discussed in the preceding paper.'

In addition to these reactions of the hydroxyl group of the carbinols it has been observed that on heating the *trans* carbinol, condensation occurs with the elimination of one mole of water from two moles of the carbinol. The condensation product distils over at 200° under 6 mm. pressure. It may have either of the following structures (the geometric isomerism will not be indicated).

$$C_6H_5CH{=}CH\text{—}CH(CH_3)\text{—}COH(CH_3)\text{—}CH{=}CHC_6H_5$$

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$$C_6H_5CH{=}CH\text{—}CH(CH_3)\text{—}CH_2\text{—}CHOH\text{—}CH{=}CHC_6H_5$$

II

On ozonization it was possible to isolate 76 3% of benzaldehyde calculated on the basis of two moles of benzaldehyde for each mole of the condensation product. This proves that the condensation did not involve the double bonds. The condensation product also formed a tetrabromide, m. p. 179°, which confirms the above conclusion. Structure I is favored due to the fact that the hydrogen atoms of the terminal methyl group of the *trans* carbinol are very unreactive. No effort was made to distinguish between the two structures. Under the same conditions the *cis* carbinol decomposed to give water and the dimer of phenylbutadiene.

II. Reactions Involving the Double Bond

An effort was made to prepare the dibromide addition compounds of the two carbinols. The conditions of bromination were widely varied but in every case decomposition occurred with the elimination of water and the formation of the tetrabromide of phenylbutadiene.

The catalytic hydrogenation of the two carbinols by means of the Adams method[5] was studied. The products of reduction of the two carbinols were found to be identical. The compound proved to be 3-hydroxy-1-phenylbutane, $C_6H_5—CH_2—CH_2—CH(OH)—CH_3$, which was identified by means of its boiling point, 105° under 6 mm. pressure, and the melting point of its phenylurethan, 114°. The identity of the reduction products of the two carbinols was definitely established by comparing the melting points of their phenylurethans.

3-Hydroxy-1-phenylbutane has been prepared before by the reduction with sodium amalgam of benzalacetone[6] and of benzylacetone.[7] Since alkaline reagents are known to cause rearrangements of such compounds, we synthesized the 3-hydroxy-1-phenylbutane by the condensation of hydrocinnamic aldehyde with methylmagnesium bromide. The 3-hydroxy-1-phenylbutane prepared in this way was identical with that reported in the literature.

The relative rates of catalytic hydrogenation of the two carbinols were determined. An apparatus designed by Muskat and Knapp[8] for the study of the rates of catalytic hydrogenation of unsaturated compounds was used. The apparatus was so designed that the pressure of the hydrogen always remained constant while the volume of the hydrogen varied. Under the same experimental conditions and with equal weights of catalyst from the same batch, the *cis* carbinol was hydrogenated more rapidly than was the *trans* carbinol. This is in perfect agreement with the work of Paal,[9] who has shown, after a detailed study of a large number of geometric isomers, that the *cis* compound is always more rapidly hydrogenated than is the corresponding *trans* isomer. Complete experimental data and graphs for the hydrogenation of each of the carbinols will be given in the Experimental Part.

The oxidation of the two carbinols with perbenzoic acid was studied. It was found that under the same experimental conditions the *cis* carbinol

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[5] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, pp 10, 92.

[6] Engler and Leist, *Ber.*, 6, 255 (1873).

[7] Klages, *ibid.*, 37, 2313 (1904).

[8] To be published soon.

[9] Paal, Ber., 60, 1221 (1927); *ibid.*, *63*, 766 (1030).

was oxidized more rapidly than was the *trans* carbinol. This same difference was also observed in the rate of oxidation with perbenzoic acid of the two geometric isomers of phenylbutadiene.[8] This suggests that it might be possible to use the relative rates of oxidation with perbenzoic acid as a means of distinguishing between geometric isomers.

Both Böeseken[10] and Meerwein[11] have attempted to calculate the velocity constants for the oxidation of unsaturated compounds by means of perbenzoic acid. They have concluded from their results that the oxidation follows a second order reaction. These conclusions seem to us to be not wholly warranted since the data show a decided decrease in the second order reaction constant as the oxidation proceeds. Thus, for the oxidation of pinene, Meerwein has calculated the following values for the second order reaction constant K

Minutes	5	10	20	40	60
$K \times 10^3$	1573	1138	985	866	845

It appears to us that these oxidation reactions are not properly expressed by the equation for a second order reaction.

We have calculated the velocity constants for the oxidation experiments reported here. After calculating K for a first, second and third order reaction, it became quite obvious that the oxidation of methylstyrylcarbinol is best expressed by the equation for a third order reaction. K_3 is remarkably constant for this type of work and is well within the experimental limits of error.

The exact significance that may be attached to this is still uncertain. It seems that the rate of oxidation of an unsaturated compound with perbenzoic acid is proportional to the concentration of the unsaturated compound and to the square of the concentration of the perbenzoic acid. Further work on the oxidation of unsaturated compounds by means of perbenzoic acid and also of peracetic acid is contemplated.

The oxides of each of the carbinols were isolated. They had approximately the same boiling points: the oxide of the *trans* carbinol distilled at 118° under 4 mm. pressure, while the oxide of the *cis* carbinol distilled at 117° under 3.5 mm. pressure. The oxide of the *trans* carbinol was prepared in larger quantity in order to study its chemical properties. A number of attempts were made to break the oxide linkage but with no success. It was heated for several hours with 2 N sulfuric acid, and in place of the expected trihydroxyphenylbutane a condensation product was obtained which was formed by the elimination of one mole of water from two moles of the oxide of the *trans* carbinol. The condensation product distilled at 200° under 4-mm. pressure. It may have either of the following two structures (the geometric isomerism will not be indicated).

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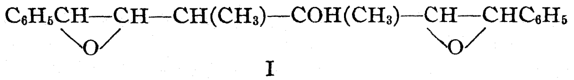
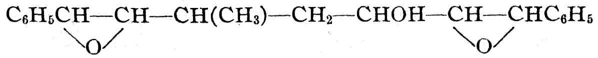
[10] Boeseken, Rec. *trav. chim.*, 44, 90 (1925).

[11] Meerwein, *J. prakt. Chem.*, **113**, 24 (1926).



$$C_6H_5\underset{\diagdown O \diagup}{CH\text{—}CH}\text{—}CH(CH_3)\text{—}COH(CH_3)\text{—}\underset{\diagdown O \diagup}{CH\text{—}CH}C_6H_5$$

I



$$C_6H_5\underset{\diagdown O \diagup}{CH\text{—}CH}\text{—}CH(CH_3)\text{—}CH_2\text{—}CHOH\text{—}\underset{\diagdown O \diagup}{CH\text{—}CH}C_6H_5$$

II

For the same reasons given above for the condensation product of the *trans* carbinol, we favor Structure I. The same condensation product was obtained on heating the oxide with dilute sulfuric acid in a bomb tube for several hours at 150°.

Dry hydrogen chloride was passed into an ethereal solution of the oxide of the *trans* carbinol. The hydroxyl group of the carbinol was attacked but the oxide linkage remained intact.

The oxide of the carbinol was heated for several hours with dilute alkali. No reaction occurred and the original oxide was'isolated.

Dry ammonia gas was bubbled through an alcoholic solution of the oxide for several hours but no reaction occurred.

This remarkable stability of the oxide linkage casts some doubt as to the presence of such a linkage in the molecule. It may be that the oxide had rearranged to a ketone in a manner normal to ethylene oxides.

$$C_6H_5\text{—}\underset{\diagdown O \diagup}{CH\text{—}CH}\text{—}CHOH\text{—}CH_3 \longrightarrow C_6H_5\text{—}CH_2\text{—}CO\text{—}CHOH\text{—}CH_3$$

It is interesting to note that different samples of the pure oxide always gave typical ketonic color reactions but every effort to prepare a derivative of such a ketone failed.

The oxide of stilbene has been found to show very much the same stability as does the oxide of the *trans* carbinol. However, the oxide of stilbene could not have undergone a rearrangement to the ketone

$$C_6H_5\text{—}\underset{\diagdown O \diagup}{CH\text{—}CH}\text{—}C_6H_5 \longrightarrow C_6H_5\text{—}CH_2\text{—}CO\text{—}C_6H_5$$

desoxybenzoin, for the properties of the two are decidedly different.

An effort was made to oxidize the methylstyrylcarbinols with potassium chlorate and osmic acid but with no success.

Experimental Part

The two methylstyrylcarbinols were prepared according to the method described in the preceding article by Muskat and Herrman.[1]

I. Reactions of the Hydroxyl Group

(a) **Phenylurethan.**—The phenylurethan of the *trans* methylstyrylcarbinol was prepared as follows. Equimolar quantities of the carbinol and of phenyl isocyanate, each dissolved in a small amount of dry ligroin, were mixed together and the solution was allowed to stand. In a few hours an oily layer settled out and crystals slowly formed in the oil. After several days the oil was completely transformed into a yellowish crystalline mass. The ligroin was poured off and the crystals were dissolved in hot benzene. After filtration the benzene was removed by vaporization. The light yellow crystalline deposit which remained was purified by several recrystallizations from hot alcohol. The pure, white crystals melted at 94°.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, **76.36;** H, **6.41;** N, **5.24.** Found: C, **76.42, 76.45; H, 6.74, 6.68; N, 5.29, 5.29.**

If the *cis* carbinol is treated in a similar manner with phenyl isocyanate, water is eliminated, and the phenyl isocyanate is converted to the crystalline carbanilide, m. p. 235°, which is insoluble in benzene. No trace of a phenylurethan could be detected.

(b) Acetate.—The acetate of the *trans* carbinol was prepared according to Burton's[3] method, by refluxing **10** g. of the carbinol with **15** cc. of acetic anhydride for six hours. An acetate which distilled at 141–144° under **15** mm. pressure, was obtained.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, **75.8;** H, **7.4.** Found: C, **75.67, 75.25;** H, **7.61, 7.57.**

It appears from these results that Burton had the *trans* carbinol but was not aware of it.

Under the same conditions the cis carbinol is dehydrated to give a preponderance of the dimer of phenylbutadiene. This was proved by analysis of the product.

(c) Chloride.—The *trans* carbinol was dissolved in approximately twice its volume of anhydrous ether, and dry hydrogen chloride was allowed to pass in until it ceased to be absorbed. The flask was immersed in an ice-bath during the reaction. The ethereal solution was then thoroughly washed with water to remove all of the acid, dried over anhydrous sodium sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure, the residual oil, with the exception of a small fraction, distilled over completely at **104°** under *6* mm. pressure.

Anal. Calcd. for $C_{10}H_{11}Cl$: **Cl, 21.29.** Found: **Cl, 21.21, 21.17.**

Under the same conditions the *cis* carbinol reacted with hydrogen chloride to give an almost quantitative yield of a chloride which distilled at 108° under 6 mm. pressure.

Anal. Calcd. for $C_{10}H_{11}Cl$: **Cl, 21.29.** Found: **Cl, 21.29, 21.43.**

It should be emphasized that for the preparation of either of the chlorides it is essential to remove all traces of acid before distillation. If any acid remains the chlorides decompose on distillation to give a tarry residue.

The *trans* chloride was refluxed with a 10% solution of sodium acetate. The reaction mixture was then extracted with ether, the ethereal solution dried over anhydrous sodium sulfate, and the ether removed by vaporization. The residual oil was distilled under diminished pressure. Two fractions were collected: (1) b. p. 118° under **4** mm. pressure, **(2)** b. p. 200° under 6 mm. pressure. These fractions were analyzed: **(1)** proved to be the acetate of the *trans* carbinol which was described above, while **(2)** was a condensation product of the *trans* carbinol which will be described later in the paper.

The *trans* chloride was refluxed with a water suspension of silver oxide until all of the chloride had reacted. The reaction mixture was then extracted 'with ether and worked up in the usual manner as described above. Two fractions were collected: **(1) b.** p. 76° under **11** mm. pressure and **(2)** b. p. **194"** under **3 mm.** pressure. Fraction 1, of which but a small amount was obtained, proved to be the *trans* phenylbutadiene, while fraction *(2)* was the polymer of the *trans* phenylbutadiene. These compounds were identified by analyses.

The *trans* chloride was refluxed with about five times its volume of dry pyridine for several hours. The reaction mixture was then taken up in ether, and the ethereal solution was thoroughly washed with water to remove all of the pyridine. The ethereal solution was dried over anhydrous sodium sulfate, and the ether was removed by vaporization. When subjected to distillation under diminished pressure, the residual oil, with the exception of a small fraction, distilled over completely at 76° under 11 mm. pressure, the boiling point of the *trans* phenylbutadiene. It was further identified by analysis.

The *cis* chloride was treated with pyridine in an analogous manner and yielded about 40% of the *cis* phenylbutadiene, b. p. 86° under 11 mm. pressure. The remainder was polymerized to the dimer, b. p. 205° under 10 mm. pressure. Both compounds were further identified by analyses.

The *trans* chloride was shaken with twice the theoretical amount of 5% sodium hydroxide for approximately twenty-four hours. The mixture was then extracted with ether, the ethereal solution thoroughly washed with water to remove the excess alkali, dried over anhydrous sodium sulfate, and the ether was removed by vaporization. The residual oil distilled almost completely at 76° under 11 mm. pressure, which is the boiling point of the *trans* phenylbutadiene.

When treated with alkali under the same conditions, the *cis* carbinol gave a very small yield of the *cis* phenylbutadiene, b. p. 86° under 11 mm. pressure, and the remainder was polymerized to the dimer. Both compounds were further identified by analyses.

(d) Condensation.—The *trans* methylstyrylcarbinol was heated to a temperature of 180° under atmospheric pressure. Droplets of water were formed on the sides of the reaction vessel and the mass became viscous and assumed a dark brown color. The viscous mass was extracted with ether, the ethereal solution dried over sodium sulfate, and the ether was removed by vaporization. The residual oil was distilled under diminished pressure. After a small amount of unchanged carbinol distilled over, the temperature rose quickly to 200°, at which point the bulk of the material distilled over under 6 mm. pressure.

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.27; H, 7.97. Found: C, 86.38, 86.17; H, 8.18, 7.76. Calcd. for $C_{20}H_{22}O$: mol. wt., 278.17. Found: mol. wt., 282.3.

The condensation product was ozonized in a manner entirely analogous to that described for the *trans* methylstyrylcarbinol in the preceding paper.[1] Five grams of the condensation product gave 2.3 g. of the semicarbazone of benzaldehyde and 1.6 g. of benzoic acid. This corresponds to a 76.3% yield of benzaldehyde on the basis of two moles of benzaldehyde for each mole of the condensation product.

A chloroform solution of the condensation product was treated with two moles of bromine, also in chloroform solution. This solution was completely decolorized, but no further absorption followed the addition of a few more drops of bromine solution. The chloroform was removed and the residual solid mass was recrystallized several times from hot ligroin. The pure bromide melted at 179°.

Anal. Calcd. for $C_{20}H_{22}OBr_4$: Br, 53.47. Found: Br, 53.55, **53.35.**

II. Reactions Involving the Double Bond

(a) **Bromination.**—A number of attempts to prepare a dibromide addition compound of the two carbinols were made but with no success. In every case decomposition occurred with the elimination of water, resulting in the formation of the tetrabromide of phenylbutadiene. This was identified by its melting point, 146°, and the melting point of a mixture with a sample of known origin. In one experiment the carbinol (in an open weighing bottle) was placed in a desiccator containing an equivalent amount of bromine, also contained in a weighing bottle. The desiccator was closed and the bromine, which vaporized slowly, reacted with the carbinol. Even under such mild conditions, decomposition of the carbinol occurred, with the formation of the tetrabromide of phenylbutadiene.

(b) Catalytic Hydrogenation.—Each of the two carbinols was hydrogenated catalytically by the Adams method.[5] The catalyst was prepared in the manner described by Adams and methyl alcohol was used as the solvent. After the hydrogenation was complete, the catalyst was removed by filtration, and the filtered solution was subjected to distillation under diminished pressure. The methyl alcohol was first removed, after which, in each instance, the temperature rose to 105° under 6 mm. pressure, and the remainder distilled over completely at this temperature.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.4. Found: C, 79.91, 79.79; H, 9.34, 9.76.

The phenylurethan of each of the reduced carbinols was prepared by merely adding an equivalent weight of phenyl isocyanate to the pure reduction products and allowing to stand for a few hours. In each case the solution solidified completely. After several recrystallizations from alcohol, the pure crystals melted at 113°, as did a mixture of the two. This proved the identity of the reduction products of the two carbinols.

The 3-hydroxy-1-phenylbutane was synthesized by condensing hydrocinnamic aldehyde with methylmagnesium bromide and decomposing the resulting addition compound with dilute acid, in a manner entirely analogous to that described by Muskat and Herrman[1] for the preparation of the *trans* carbinol. The 3-hydroxy-1-phenylbutane, prepared in this manner, also distilled at 105° under 6 mm. pressure, and gave a phenylurethan which melted at 113° and did not lower the melting point of the above phenyl urethans when mixed with it.

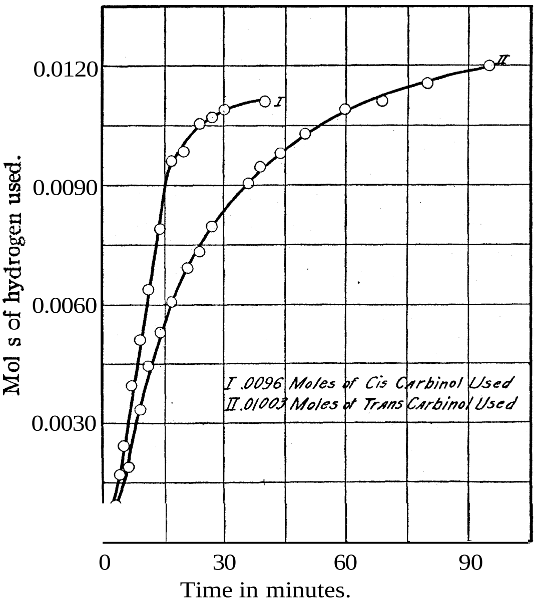


Fig. 1.—50 cc. of glacial acetic acid used as solvent.

(c) The Relative Rate of Catalytic Hydrogenation of the Two Isomeric Carbinols.—The apparatus and method used in determining the rates of catalytic hydrogenation will be described in detail in a paper to be published soon by Muskat and Knapp.

Ten-milligram portions of the same batch of the catalyst were used in all of the experiments. The barometric pressure was 747 mm. and the temperature was 29° except in the case of the *trans* methylstyrylcarbinol in glacial acetic acid, where it was 744 mm. and the temperature 27°. The excess pressure in every case was 88 cm. The experimental data obtained are given graphically in Figs. 1 and 2.

(d) Oxidation of the Methylstyrylcarbinols with Perbenzoic Acid.—Each of the two isomeric carbinols was oxidized with perbenzoic acid. The perbenzoic acid was prepared according to the method of Tiffeneau.[12] The carbinols, dissolved in chloroform, were treated with a chloroform solution of perbenzoic acid following the method

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[12] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 30.

first used by Prileshajew[13] for the oxidation of unsaturated compounds. The rate of oxidation was easily followed by the usual iodimetric titration. The rates of oxidation of the two carbinols were determined at different temperatures and with different concentrations of perbenzoic acid. A blank on the perbenzoic acid was always run concurrently with each of the oxidation experiments. Only those runs are included here in which the blank was negligible. At definite time intervals 2 cc. of the solution was removed, added to an acidified solution of potassium iodide, and the liberated iodine was titrated with standard sodium thiosulfate solution.

Previous investigators, who determined the rate of oxidation of unsaturated compounds by means of perbenzoic acid, have experienced considerable difficulty in obtaining reproducible results. Thus Boeseken and Blumberger[14] state that some unknown catalytic effect influenced the rate of oxidation. They state further that oxidation occurs more readily with perbenzoic acid that has been allowed to age than with freshly prepared perbenzoic acid. Meerwein,[15] on the other hand, reports directly conflicting results. During our study of the rate of oxidation of the two carbinols we were able to prove conclusively that the inconsistent results first obtained were not due, in this particular case, to any variation in the perbenzoic acid but rather to the method of titration. When the sample (2 cc.) that was taken out for titration was added to the dilute acetic acid solution of potassium iodide, iodine was set free. If this mixture is allowed to stand before titration, the iodine is absorbed by the unsaturated compound and a much lower titer is obtained. For unsaturated compounds that are but slowly oxidized, such a lowering of the titer may easily change the data by 100%. Consequently in all of the data given here the iodine that was set free was immediately titrated. If this precaution was taken it was easily possible to duplicate our results. The graphs for the oxidation of the two isomeric methylstyryl carbinols are given in Fig. 3.

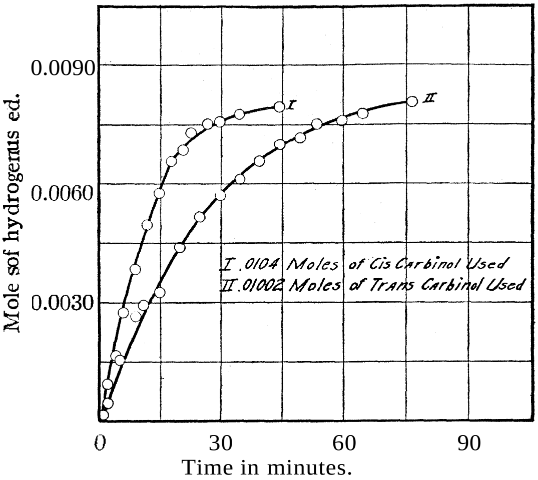

Fig. 2.—50 cc. of CH_3OH used as solvent.

We have calculated the velocity constants for the oxidation experiments reported here. Since the initial molar concentrations of the perbenzoic acid and of the carbinols were very nearly equal, we were able to use the following set of equations for the determination of the velocity constants.

$$\text{First order:} \quad K_1 = \frac{2.303}{t} \log \frac{A}{(A - x)}$$

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[13] Prileshajew, *Ber.*, **42**, 4811 (1909). See also Nametkin and Brussoff, *J. prakt. Chem.*, **112**, 169 (1926); Meerwein, *ibid.*, **113**, 9 (1926); Böeseken, *Rec. trav. chim.*, **47**, *683* (1928); ibid., **48**, 363 (1929).

[14] Boeseken and Blumberger, *ibid.*, 44, 90 (1925).

[15] Meerwein, *J. prakt. Chem.*, **113**, 24 (1926).

$$\text{Second order:}\quad K_2 = \frac{1}{t}\,\frac{1}{(A - x)} - \frac{1}{A}$$

$$\text{Third order:}\quad K_3 = \frac{1}{2t}\,\frac{1}{(A - x)^2} - \frac{1}{A^2}$$

A is initial concentration of perbenzoic acid and of the carbinol; $(A - x)$ is concentration of perbenzoic acid at time t.

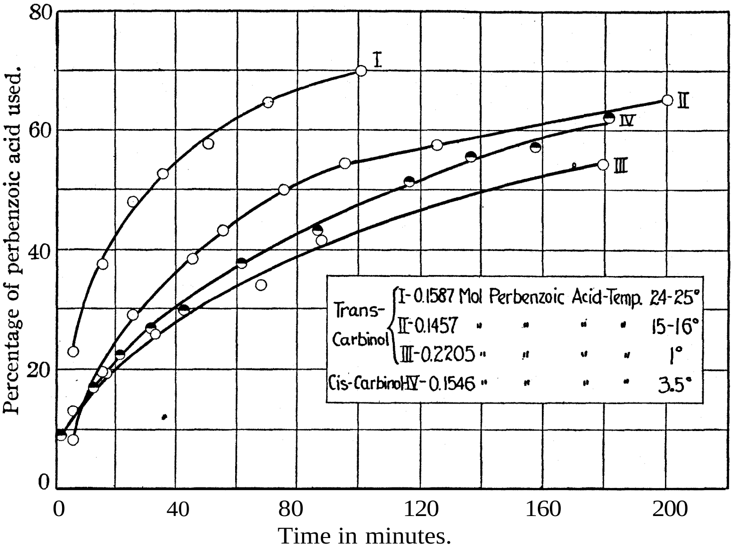

Fig. 3.

Trans Methylstyrylcarbinol, 1.—Twenty-two grams of sample; total volume of solution, 950 cc.; temp., 24–25°; $Na_2S_2O_3$, 0.1100 N.

A = 0.1587 mole per liter. $(A - x) = 0.0275 \times$ cc. of $Na_2S_2O_3$

Minutes	0	5	15	25	35	50	70	100
$Na_2S_2O_3$, cc.	5.77	4.68	3.65	3.00	2.75	2.44	2.07	1.81
K_1	..	0.042	0.031	0.026	0.021	0.017	0.015	0.012
K_2	..	0.294	0.245	0.233	0.198	1.61	0.72	0.138
K_3	..	2.07	2.00	2.14	1.94	1.82	1.93	1.82

K_3 (average) = 1.96 Average deviation, 4.8%.

Trans Methylstyrylcarbinol, 11.—Seventeen grams of sample; total volume of solution, 800 cc.; temp., 15–16°; $Na_2S_2O_3$, 0.1100 N.

A = 0.1457 mole per liter. $(A - x) = 0.0275 \times$ cc. of $Na_2S_2O_3$

Minutes	0	5	15	25	45	55	75	95	125	200
$Na_2S_2O_3$, cc.	5.30	4.85	4.25	3.75	3.25	3.00	2.65	2.50	2.25	1.85
K_1	..	0.0176	0.0147	0.0138	0.0109	0.0104	0.0092	0.0087	0.0069	00.053
K_2	..	0.127	0.113	0.113	0.096	0.096	0.091	0.0807	0.074	0.064
K_3	..	0.909	0.869	0.939	0.867	0.907	0.940	0.865	0.856	0.848

K_3 (average) = 0.889. Average deviation, 3.5%.

Trans Methylstyrylcarbinol, III.—Thirty grams of sample; total volume of solution, 970 cc.; temp., 1°; $Na_2S_2O_3$, 0.1100 N.

$A = 0.2205$ mole per liter. $(A - x) = 0.0275 \times$ cc. of $Na_2S_2O_3$

Minutes	0	16.5	32.5	67.5	87.5	179
$Na_2S_2O_3$, cc.	8.02	6.53	5.93	5.26	4.59	3.65
K_3	..	[0.316]	0.262	0.202	0.241	0.219

K_3 (average) = 0.231. Average deviation, 8.9%

Cis Methylstyrylcarbinol, IV.—Eighteen and three-tenths grams of sample; total volume of solution, 800 cc.; temp., 3.5°; $Na_2S_2O_3$, 0.1014 N.

$A = 0.1546$ mole per liter. $(A - x) = 0.02535 \times$ cc. of $Na_2S_2O_3$

Minutes	0	21	31	42	61	86	116	136	157
$Na_2S_2O_3$, cc.	6.10	4.75	4.45	4.28	3.80	3.45	2.95	2.70	2.60
K_3	..	0.642	0.593	0.513	0.540	0.516	0.590	0.631	0.599

K_3 (average) = 0.578. Average deviation, 7.14%.

Summary

1. The chemical reactions of the two geometric isomers of methylstyrylcarbinol were studied. These studies included the reactions involving the hydroxyl group and the double bond The differences in the reactivity of the two carbinols were noted in each case.

2. The relative rates of catalytic hydrogenation of the two isomeric carbinols were determined. The *cis* carbinol was reduced more rapidly than the corresponding *trans* carbinol.

3. The relative rates of oxidation of the two isomeric carbinols by means of perbenzoic acid were determined. The *cis* carbinol was oxidized more rapidly than the corresponding *trans* carbinol.

4. The velocity constants for these oxidation reactions were calculated and it was found that the rate of oxidation of the two carbinols is best expressed by the equation for a third order reaction.

5. The oxides of the two carbinols were prepared and their reactions studied.

CHICAGO, ILLINOIS

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

ADDITION OF PHENOLS TO THE ETHYLENIC LINKAGE.[1] REACTION MECHANISM AND SYNTHESIS OF CERTAIN PHENOLIC ETHERS

BY JOSEPH B. NIEDERL AND SAMUEL NATELSON

RECEIVED OCTOBER 25, 1930 PUBLISHED JANUARY 12, 1931

Theoretical Part

Isolated cases of reactions between phenols and unsaturated compounds have been reported before. Isoprene,[2] cinnamic acid,[3] cyclohexene,[4] isoamylene, styrene[5] and acetylene[6] have been condensed with phenol type compounds under the influence of mineral acid with the formation of the corresponding substituted phenol in most cases.

In 1925 Niederl[7] showed that acetone condenses with phenols and that the resulting compounds could also be obtained by the interaction of unsaturated ketones with phenols. The reaction was shown to be an addition of the phenol to the unsaturated ketone.[8] This reaction was then systematically studied and it was found that the following types of unsaturated compounds would condense with phenols: alcohols,[9] ethers,[10] esters,[11] aldehydes,[12] ketones,[13] acids,[14] nitriles, amines, halides and ethylene oxide.[15]

The purpose of the present research was to continue the work on into the unsaturated hydrocarbon series in order to study the products obtained

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[1] Constructed from part of the thesis presented by Samuel Natelson to the Faculty of the Graduate School of New York University in candidacy for the degree of Doctor of Philosophy, **1931.** This research was presented at the Cincinnati meeting of the American Chemical Society.

[2] Claisen, German Patent **374,142 (1923).**

[3] Liebermann and Hartmann, *Ber.*, 24, **2582 (1891);** 25, **957 (1892).**

[4] Schrauth and Quasebarth, *ibid.*, 57, **854 (1924).**

[5] König, *ibid.*, 24, **3889 (1891).**

[6] Wenzke and Nieuwland, THIS JOURNAL, 46, **177 (1924).**

[7] Niederl, "Inaugural Dissertation," University of Graz, Austria, April, **1925;** compare Jordan, Schering-Kahlbaum, British Patents **279,855, 279,857, 280,924 (1928);** Canadian Patents **281,114, 281,120 (1928).**

[8] Niederl, THIS JOURNAL, 50, **2230 (1928);** Niederl and Casty, *Monatsh*, 51, **1038 (1929).**

[9] Niederl and McGreal, Columbus Meeting, American Chemical Society, **1929.**

[10] Storch, Sc.M. Thesis, New York University, **1930.**

[11] Adams, Sc.M. Thesis, New York University, **1930.**

[12] Niederl, Smith and Wilson, Columbus Meeting, American Chemical Society, **1929.**

[13] Niederl, THIS JOURNAL, 51, **2426 (1929);** Knowles, Sc.M. Thesis, New York University, **1929;** Sen and Quadrat-I-Khuda, J. *Indian Chem. Soc.*, 7, **167 (1930).**

[14] Liebermann and Hartmann, *Ber.*, 24, **2582 (1891);** 25, **957 (1892).**

[15] Work is now in progress at New York University.

with a view toward a probable mechanism for all these condensation reactions with phenols.

β-Amylene and di-isobutylene were treated with phenol and the cresols in the presence of sulfuric acid. The corresponding ethers were obtained. The following mechanism is offered for this reaction, taking the reaction between β-amylene and m-cresol as an example.

It is first assumed that sulfuric acid is added to the unsaturation of amylene.[16] An ester would be formed of the structure

$$CH_3CH_2CH{=}CHCH_3 + H_2SO_4 = CH_3CH_2CH_2CH(CH_3)OSO_3H$$

Since condensation took place, it could only have taken place in one of two ways: either in the formation of a five carbon substituted phenol, or in an elimination of sulfuric acid with the formation of an amyl cresyl ether

$$CH_3CH_2CH_2CH(CH_3)\boxed{OSO_3H + H}OC_6H_4(CH_3) = CH_3CH_2CH_2CH(CH_3)OC_6H_4(CH_3)$$

This ether had not been reported in the literature up to this time and the proof of its structure was therefore undertaken. It was synthesized according to the Williamson method.[17] The resulting compound was shown to be identical with the ether obtained using the condensation method.

It appears from the work accomplished that the condensation of unsaturated ketones, alcohols, ethers, esters, aldehydes, acids and hydrocarbons (where the reactions are carried out at higher temperatures) takes a different course than the condensation of unsaturated hydrocarbons with phenols in the cold, substituted phenols being obtained in the first case and ethers in the latter. An explanation was then sought which would harmonize these differences. Claisen[18] and others[19] have shown that alkyl phenyl ethers with a negative group in the alkyl radical are prone to rearrange upon heating or, more rapidly, in the presence of mineral acid or zinc chloride. The formation of substituted phenols upon condensation of unsaturated alcohols, ethers, esters, aldehydes, ketones and acids with phenols can now be better explained. Addition of sulfuric acid is first assumed and then elimination of the acid with the formation of an ether. Ethers of these types, as mentioned above, have been shown to rearrange rapidly, especially in the presence of mineral acids. Under the conditions of the experiment, therefore, the ether was not isolated, but the substituted phenol was obtained.

In the condensation of amylene and di-isobutylene with phenols in the cold, ethers were formed with a saturated alkyl group. These are known

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[16] Wurtz, *Ann.*, 125, 118 (1863).

[17] Williamson, *J. Chem. Soc.*, *4*, 106 (1851).

[18] Claisen, *Ann.*, 237, 261 (1887); 401, 21, 119 (1914); *Ber.*, 45, 3157 (1912); 58, 275 (1925); *Z. angew. Chem.*, 36, 478 (1923).

[19] Van Alphen, *Rec. trav. chim*, 46, *799* (1927); Heller, *Ber.*, 45, 418 (1912); Bucherer and Grolée, *ibid.*, 39, 986 (1906); Kursanov, *J. Russ. Phys.-Chem. Soc.*, 48, 1172 (1914); Eijkman, *Chem. Zentr.*, *I*, 1597 (1904); I, 814 (1905).

to be stable and will not rearrange except under unusual conditions. It was therefore of interest to see whether these long-chain ethers would rearrange at higher temperatures. This would explain the substituted phenols obtained by Konig and Schrauth, by condensing unsaturated hydrocarbons at higher temperatures. o-Cresyl di-isobutyl ether was therefore gently refluxed for five hours in the presence of a mixture of zinc chloride and hydrochloric acid. A crystalline solid was obtained which was shown to be di-isobutyl o-cresol

$$(CH_3)C_6H_4OC_8H_{17} \xrightarrow{\text{Rearrangement}} (CH_3)C_6H_3(C_8H_{17})OH$$

The mechanism then proposed for all these condensations of unsaturated compounds with phenols would constitute an addition of hydrogen sulfate to the ethylenic linkage and a subsequent elimination of the acid with the formation of an ether. This ether in the case of saturated alkyl chains is stable and will not rearrange. In the case of more negative or heavier groups, rearrangement takes place with the formation of the corresponding substituted phenol.

Experimental Part

Condensation Method.—The method followed in these condensations is based upon work reported in earlier articles.[20]

One molecular weight of the cresol or phenol was weighed into a 500-cc. Erlenmeyer flask. To this was added one mole of the unsaturated hydrocarbon, care being taken to avoid excessive evaporation. The flask was well corked and the contents shaken until complete solution had taken place. The mixture was surrounded by an ice and salt bath and allowed to come to zero degrees. Ninety-eight grams of sulfuric acid was weighed out and transferred to a buret. Two drops of sulfuric acid were carefully added. The cork was replaced and the flask thoroughly shaken, keeping the whole immersed in the freezing mixture. The remaining sulfuric acid was then added drop by drop with constant stirring and shaking. At no time was the temperature allowed to go over zero degrees. If this precaution is not observed side reactions are favored and a marked decrease in the yield is noticed. After half of the sulfuric acid has been added further addition does not increase the temperature greatly and the remainder can be added fairly rapidly.

The flask was then stoppered with a cork through whose bore was placed a calcium chloride drying tube to exclude moisture and to allow any gases formed to escape. The mixture, which was almost colorless and mobile at first, turned a pink, brown or red color on standing, dependent upon the phenol or cresol used, and assumed a heavy viscous appearance. The flask was allowed to remain in the bath until the ice had melted, and then after shaking was allowed to stand for one week at room temperature with occasional shaking. The viscosity seemed to increase slowly until it reached a constant value after four or five days.

The mixture was loosened from the walls of the vessel with ice water. Five molar, ice cold, sodium hydroxide was then added until the whole solution was just alkaline. On standing an oil separated at the top of the liquid. This was removed in a separatory funnel. In some cases it was more convenient to extract with ether and then evaporate the ether on a water-bath.

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[20] Niederl, THIS JOURNAL, 50, 2230 (1928); 51, 2426 (1929).

The separate oil was washed twice with 50-cc. portions of dilute alkali (5%). It was then washed with two 50-cc. portions of saturated salt solution and then with 25 cc. of distilled water.

The liquid was dried over anhydrous potassium carbonate overnight, then transferred to an Erlenmeyer flask and a few bright pieces of sodium were introduced. After being left overnight effervescence ceased and the liquid was then distilled over a small piece of sodium. This precaution was necessary to remove the last traces of cresol or amyl alcohol, which may have been formed in the reaction as a by-product. The distillate thus obtained was then fractionated several times.

s-Amyl *m*-Cresyl Ether, 2-m-Cresoxypentane, $CH_3CH_2CH_2CH(CH_3)OC_6H_4(CH_3)$.—This compound was obtained by applying the above method to amylene (b. p. 35–37°) and m-cresol. The fraction first collected was between 210–245°. Upon redistillation most of the liquid came over between 235–238°. The material was a clear mobile liquid which had a faint aromatic odor: b. p. 238° (uncorr.); n_D^{21} 1.500; sp. gr. 0.920 (20").

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.89; H, 10.11; mol. wt. 178. Found: C, 80.57; H, 10.77; mol. wt. 179.6.

The above ether was nitrated, using the following method: 20 cc. of concentrated sulfuric acid was mixed with 1 cc. of the condensation product. Concentrated nitric acid was added drop by drop until the vigorous reaction had ceased; 5 cc. was added in excess and the whole warmed on a water-bath until brown fumes ceased to be given off.

The reaction mixture was then poured into 200 cc. of water, when a yellowish-brown precipitate came out on standing. The precipitate was washed with water, a limited quantity of dilute sodium bicarbonate solution and then again with small portions of water. The brown mass was dried on a porous plate and recrystallized from 75% alcohol.

The material on recrystallization gave dark brown needles melting at 106°, which was shown to be trinitro-m-cresol. This product is probably formed on hydrolysis of the ether by the sulfuric acid and then nitration of the freed cresol.

Anal. Calcd. for $C_7H_5N_3O_7$: N, 17.29. Found: N, 17.01.

s-Amyl m-cresyl ether was also prepared by the following method:[21] 14 g. of sodium was dissolved in 200 cc. of absolute ethyl alcohol in a three-necked flask fitted with a reflux condenser. While the last bit of sodium was dissolving, 65 g. of m-cresol was added through a dropping funnel. The whole was refluxed for twenty minutes. Through the same dropping funnel extending below the level of the liquid, amyl bromide prepared by the method of Wurtz[16] was added drop by drop with constant refluxing. After all the halide had been added, refluxing was continued for two hours more. Sodium bromide separated out in less than twenty minutes and the flame had to be kept low to avoid excessive bumping. At the end of two hours the flask was allowed to cool and its content filtered with suction from the separated sodium bromide. The filtrate was put in a distilling flask and the alcohol distilled off.

The oil was separated from more sodium bromide, which had come out, by extraction with ether. The ether extract was washed with dilute sodium hydroxide solution, then with water and dried over calcium chloride. It was next treated with metallic sodium to remove any alcohol or cresol still left. The ether was evaporated and the oil fractionated. The major portion came over between 234–238°: b. p. 238" (uncorr.); n_D^{21} 1.496; sp. gr. 0.915 (20°).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.89; H, 10.11. Found: C, 80.82; H, 10.11.

On nitrating, as described before, trinitro-m-cresol was also obtained.

By applying the procedure given for amylene and m-cresol to phenol and the other cresols the following products were obtained.

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[21] Williamson, J. *Chem. Soc.*, 4, 106 (1851).

***s*-Amyl *p*-Cresyl** Ether, **2-*p*-Cresoxypentane,** $CH_3CH_2CH_2CH(CH_3)OC_6H_4(CH_3)$.—The crude product distilled between 220–240°. This on careful redistillation gave a product which boiled fairly constantly between 223–225"; b. p. 225 (uncorr.); sp. gr. 0.920 (20°); n_D^{21} 1.505.

***s*-Amyl** o-Cresyl Ether, 2-o-Cresoxypentane, $CH_3CH_2CH_2CH(CH_3)OC_6H_4(CH_3)$.—The crude product distilled between 210–240°. On fractionation most of the material came over between 231–234"; b. p. 234°; n_D^{21} 1.493; sp. gr. 0.915 (20°).

The application of the condensation process to di-isobutylene, phenol and the cresols yielded the following products.

Di-isobutyl Phenyl Ether, **2,2,4-Trimethyl-4-phenoxypentane,** $CH_3C(CH_3)_2CH_2C(CH_3)_2OC_6H_5$.—The material obtained was a clear, colorless liquid which solidified to needle-like crystals on prolonged cooling in an ice and salt bath. The material distilled with slight decomposition at atmospheric pressure. It distilled at 190° at 40 mm.; m. p. 12°; b. p. 258° (760 mm.); 190" (40 mm.); sp. *gr.* 0.950 (20°); n_D^{21} 1.510.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.55; H, 10.68. Found: C, 80.49; H, 10.47.

By applying the Williamson method to di-isobutyl bromide prepared by the method of Kondakow[22] and sodium phenolate, an ether was obtained which showed the following physical constants: m. p. 11°; b. p. 193° (40 mm.); n_D^{21} 1.505; sp. *gr.* 0.930 (20").

On nitration of di-isobutyl phenyl ether after the method described under amyl-*m*-cresyl ether, a product was obtained which melted at 120° and was shown to be picric acid by a mixed melting point. This product was obtained from both the condensation product and the synthesized ether.

p-Cresyl Di-isobutyl Ether, **2,2,4-Trimethyl-4-*p*-cresoxypentane,** $CH_3C(CH_3)_2CH_2C(CH_3)_2OC_6H_4(CH_3)$.—A clear liquid was obtained which was purified by fractionation: b. p. 272° (uncorr.); n_D^{21} 1.470; sp. gr. 0.889 (20°).

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.82; H, 10.91. Found: C, 81.65; H, 10.91.

m-Cresyl **Di-isobutyl** Ether, **2,2,4-Trimethyl-4-*m*-cresoxypentane,** $CH_3C(CH_3)_2CH_2C(CH_3)_2OC_6H_4(CH_3)$.—The crude oil distilled from 250–275". On fractionation the portion from 269–273° was collected; b. p. 273° (uncorr.); sp. gr. 0.895 (20°); n_D^{21} 1.476.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.82; H, 10.91. Found: C, 81.99; H, 11.12.

Di-isobutyl o-Cresyl Ether, **2,2,4-Trimethyl-4-*o*-cresoxypentane,** $CH_3C(CH_3)_2CH_2C(CH_3)_2OC_6H_4(CH_3)$.—B. p. 271" (uncorr.); m. p. 6° (uncorr.); sp. gr. 0.881 (20"); n_D^{21} 1.472.

Di-isobutyl *o*-Cresol, $CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_3(CH_3)OH$.—Hydrogen chloride was bubbled through 20 g. of di-isobutyl o-cresyl ether at zero degrees until 0.5 g. increase in weight was observed; 1 g. of anhydrous zinc chloride was added and the whole heated in an oil-bath to 200° for five hours. The mixture was steam distilled. An oil separated out which solidified to needle-like crystals on cooling. The phenolic properties of the compound are illustrated by its reaction with aqueous sodium hydroxide solution (formation of a soap-like sodium salt, soluble in water with difficulty) and of its alcoholic solution with ferric chloride with the formation of a transient green color; m. p. 49–50" (uncorr.).

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.82; H, 10.91. Found: C, 82.17; H, 10.37.

Summary

The condensation of unsaturated hydrocarbons with phenolic type compounds was carried out. Ethers were obtained. This work, therefore, affords a method of preparing certain alkyl phenyl ethers.

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[22] Kondakow, J. *prakt.* Chem., [2] *54*, 450 (1897).

A mechanism was proposed not only for this condensation reaction but also for all similar condensation reactions between compounds containing the ethylenic linkage and phenols in the presence of sulfuric acid.

Further work, as to the condensation possibilities of unsaturated hydrocarbons, mono- and di-olefins, alcohols, (esters, ethers), aldehydes (acetals) and ketones, acids, nitriles, amines and halides with mono- and polyhydroxy phenols is being carried out.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

NEONICOTINE AND ISOMERIC PYRIDYLPIPERIDINES[1]

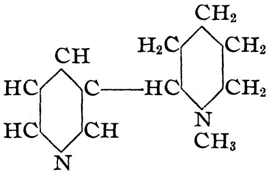
BY C. R. SMITH

RECEIVED OCTOBER 27, 1930 PUBLISHED JANUARY 12, 1931

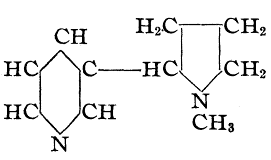
In a previous publication[2] on the interaction of sodium, pyridine and oxygen, the principal products isolated by the procedure outlined were γ,γ-, α,α-, β,γ- and β,β-dipyridyls. Later work has shown that, in addition to these compounds, there are formed water-insoluble bases boiling between 200 and 270°, richer in hydrogen than the dipyridyls, and a water-soluble base of especial interest which has been isolated and identified as β-pyridyl-α-piperidine. This compound has been called "neonicotine" because of its resemblance to nicotine in chemical structure and its toxicity to aphids and other soft-bodied insects.[3]

Neonicotine, $C_{10}H_{14}N_2$, resembles nicotine in structure more than does any of the other isomeric pyridylpiperidines. It is the only one of the pyridylpiperidines that has yet been prepared which shows any marked toxicity to insects.

A comparison of the formulas of neonicotine and nicotine reveals the similarity in structure. The N-methylneonicotine is shown in Formula I for comparison with nicotine (II)



Methylneonicotine I



Nicotine II

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[1] Presented as a part of the Insecticide Symposium before the Division of Agricultural and Food Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Georgia, April 7 to 11, 1930.

[2] C. R. Smith, THIS JOURNAL, 46,414 (1924).

[3] Toxicity results are to be reported elsewhere in a joint publication with Dr. C. H. Richardson and H. H. Shepard.

Pictet and Rotschky[4] reported the alkaloids nicotelline, nicoteine and nicotimine, in addition to nicotine, as being present in the tobacco plant. They suggested that nicotelline, $C_{10}H_8N_2$, was possibly an unknown dipyridyl. This must be incorrect since all the dipyridyls are now known, and the properties of nicotelline do not agree with any of them. Nicotimine, $C_{10}H_{14}N_2$ was described as an oil boiling at 250–255°, forming a picrate which crystallizes in thick prisms melting at 163°. It was suggested that nicotimine might be β-pyridyl-α-piperidine, which is the constitution ascribed by the author to neonicotine. Neonicotine boils at 280–282°, forms a picrate which melts at 213° (corr.) and crystallizes from water in prismatic needles. The two substances are evidently different.

There are nine possible pyridylpiperidines. The γ,γ-derivative, called isonicotine, was first prepared by Weidel and Russo.[5] The β,β-derivative, nicotidine, was prepared by Skraup and Vortmann.[6]

To these are now added the α,α, one β,γ and the two α,β-derivatives (one of which is neonicotine) prepared in this study.

Attempts to synthesize neonicotine directly from α,β-dipyridyl have usually resulted in the production of α-pyridyl-β-piperidine or isoneonicotine. It is plausible to assume that neonicotine is formed in the sodium, pyridine and oxygen reaction by some secondary reduction of α,β-dipyridyl, in spite of the fact that the author has been unable actually to separate and identify that dipyridyl. But this failure might well be ascribed to its complete reduction or the difficulties encountered in its detection. Also, attempts to increase the yield of neonicotine by the preliminary addition of α,β-dipyridyl to the sodium reaction have not as yet succeeded.

Weidel and Russo, using a different sodium–pyridine reaction, reported the presence of isonicotine. There is no indication according to the author's method of any pyridylpiperidine other than neonicotine being formed. If present, certain of these, including isonicotine, would undoubtedly appear in the neonicotine fraction as separated by the methods used.

Neonicotine has been shown to be a reduced α,β-dipyridyl because reduction with hydrogen using platinum as catalyst leads to α,β-dipiperidyl. Tin and hydrochloric acid reduction of α,β-dipyridyl leads to the formation of isoneonicotine, which is shown to be α-pyridyl-β-piperidine because it readily forms picolinic acid on oxidation with alkaline permanganate. Neonicotine would be expected to oxidize to nicotinic acid but seems to be oxidized to an intermediate product which resists complete oxidation to the acid: This oxidation will be still further studied. All the pyridylpiperidines that have been prepared except isonicotine are liquids which fume in air more readily than the dipyridyls. When warmed their odor

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[4] Pictet and Rotschky, Ber., 34, 696 (1901).

[5] Weidel and Russo, Monatsh., 3, 851 (1882).

[6] Skraup and Vortmann, *ibid.*, 4, 597 (1883).

is usually suffocating, suggesting nicotine to a certain extent. The freshly distilled oil on standing develops a sperm-like odor. Isonicotine, however, has a pleasant odor (resembling commercial opium according to Weidel and Russo). The hydrochlorides of the pyridylpiperidines are hygroscopic and are soluble in alcohol, whereas those of the dipyridyls and dipiperidyls are insoluble. The bases themselves are soluble in water in all proportions and are not extracted by ether unless strongly alkaline. When completely dried all are soluble in ether. α-Pyridyl-α-piperidine is the most soluble in ether; neonicotine is the most difficult to extract from alkaline media.

The pyridylpiperidines undergo some decomposition on distillation at atmospheric pressure, whereas the dipyridyls and dipiperidyls are unaffected. The picrates of the pyridylpiperidines crystallize well from hot water and melt with little or no decomposition, thus differing from the dipiperidyls, which usually decompose before the melting point is reached (α,β-dipiperidyl is excepted). Their nitroso derivatives all appear to be non-crystalline except nitroso-isonicotine, and are of little use in identification but may be used in freeing the pyridylpiperidines from the dipyridyls. This separation can also be effected satisfactorily by the absolute alcohol–hydrochloric acid method as used for neonicotine.

The tin reduction method of preparing the pyridylpiperidines is not satisfactory except in the case of isonicotine. Experiments that have been made with sodium reduction show that in all probability reduction to dipiperidyl is never complete but that some hexahydro product is formed along with considerable unaltered dipyridyl and tar. New methods of reduction are being tried in the hope of obtaining better yields and purer products with less manipulation.

Experimental

Isolation of Neonicotine.—Twenty-five grams of sodium, cut in thin slices, was treated with 700 cc. of dry pyridine (b. p. 115°) at room temperature for twenty-four hours or longer until the sodium had completely reacted, forming sodium dipyridine. The mixture was then digested for ten hours at 115°, cooled, and oxidized with dry oxygen at 90° until the black color had completely changed to brown with no lumps remaining. Twenty-five cubic centimeters of water and 400 cc. of ether were then added to the mixture, which was maintained at a temperature below the boiling point of ether. After standing, the sodium hydroxide tarry liquor slowly settled out, permitting decantation of the pyridine–ether layer. Fresh quantities of ether were added to the residue until it was essentially free of pyridine and soluble oils. After the pyridine and ether were removed by distillation from an oil-bath, the oil residue was distilled in a vacuum until a slight decomposition and darkening of the distillate was apparent. The dipyridyl mixture containing the neonicotine was next treated with an excess of hydrochloric acid and evaporated with 95% alcohol to separate γ,γ-dipyridyl dihydrochloride. After the dihydrochloride was filtered off, fresh additions of 95% alcohol were made and evaporation repeated until nearly all the γ,γ-dipyridyl had been removed. The alcohol was next removed from the filtrate by evaporation, and the bases were freed by caustic soda. Most of the oily layer was removed mechanically and the remainder extracted with ether. The combined oil and ether extractions were dried with solid caustic and distilled in a vacuum, the water, pyridine and alcohol in the first part of the distillation being rejected. The distilled oil was dissolved in ether, and the water-soluble dipyridyls and neonicotine were washed out with several small portions of water. The ether contained principally α,α-dipyridyl and the oils boiling below 270" contained a little β,γ-dipyridyl, and some unidentified oils boiling above 305°.

The water-soluble oils and neonicotine were evaporated with a slight excess of hydrochloric acid to low volume, freed by caustic soda, and dried in ethereal solution. The ether was removed and the oils were distilled in *vacuo*. In order to remove the water-soluble dipyridyl, principally the β,γ, the distillate was dissolved in absolute alcohol and then absolute alcohol saturated with dry hydrochloric acid gas was added to precipitate the dipyridyls. In all about 300 cc. of alcohol was required, and complete precipitation was insured by passing hydrochloric acid gas through the mixture. The filtrate was evaporated until the alcohol was removed and the impure neonicotine was then liberated with caustic soda.

The neonicotine was extracted with ether only when completely dried with lumps of caustic soda or potash. The ether was removed and the residue containing neonicotine distilled first in vacuum to remove traces of water, pyridine, etc., and then under atmospheric pressure, being collected between 275 and 285°. In order further to purify the neonicotine it was necessary to form the picrate first in alcohol solution and to recrystallize it from water. The neonicotine picrate formed prismatic needles melting at 213° (corr.). The base obtained from the picrate after careful drying boiled at 280–281° at 775 mm. pressure.

Neonicotine picrate is very insoluble in 95% alcohol, but digestion with several portions of boiling alcohol probably dissolves contaminating dipyridyl picrates from the impure picrate, causing it to become hard instead of oily. Water is excellent for recrystallizing the neonicotine picrate as well as all the other picrates of the pyridylpiperidines.

The first impure preparations of neonicotine that were prepared analyzed low in hydrogen, but as the methods of separation were improved the hydrogen content reached 7.9 to 8.8%. Considerable difficulty was encountered in low carbon determinations but this was overcome by using platinum asbestos catalyst and burning slowly in oxygen.

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.07; H, 8.64; N, 17.33. Found: C, 73.69; 7421; H, 8.30, 7.94; N (Dumas), 17.7.

Reduction of Neonicotine.—Neonicotine was hydrogenated in dilute hydrochloric acid solution, with the Adams–Vorhees platinum catalyst. The theoretical for 6H is 3.7%; the absorption found ranged between 3.9 and 4.0%. The filtered solution was concentrated, the base liberated and extracted with alcohol–ether mixture, and a weighed portion of the purified base was titrated with standard acid. The results agreed closely with the titration of dipiperidyl.

Neonicotine obtained from the picrate was reduced with hydrogen and the boiling point of the dipiperidyl was found to be 269–270°, the same as α,β-dipiperidyl. The nitroso derivative of the dipiperidyl melted at 88°. The melting point was unchanged when the substance was mixed with pure dinitroso-α,β-dipiperidyl (m. p. 88°). The dipiperidyl picrate melted at 225° and was unchanged by admixture of α,β-dipiperidyl picrate. Neonicotine is thus shown to be a hexahydro-α,β-dipyridyl. It might be rither β-pyridyl-α-piperidine or α-pyridyl-β-piperidine.

α,β-Dipyridyl.—The preparation of α,β-dipyridyl followed the procedure previously described[7] except that it has been very much simplified by the elimination of the

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[7] C. R. Smith, THIS JOURNAL, 52, 397 (1930).

lead acetate precipitation which was followed by hydrogen sulfide to remove the lead. In the improved method the solution of the potassium dicarboxylate of the α,β-dipyridyl, after filtration of the manganese dioxide, is evaporated to low volume and acidulated with hydrochloric acid until congo-red paper is just turned blue. This assures the proper hydrogen-ion concentration to precipitate quantitatively the dicarboxylic acid If too much acid is used, alkali may be added, followed carefully by acid until the indicator just changes color. The precipitated acid can be obtained very pure by dissolving in boiling water, decolorizing with carbon and evaporating to low volume.

Reduction of **α,β-Dipyridyl.**—When α,β-dipyridyl was reduced with tin and hydrochloric acid, it was found that only a part was reduced to the hexahydro compound. In the reduction experiments four to five parts of tin were used to one of dipyridyl in a large excess of hydrochloric acid. After removal of the hydrochloric acid by evaporation on the steam-bath, the addition of water always disclosed an insoluble portion of double chloride of tin and unreduced α,β-dipyridyl. These precipitates can be filtered off and reduced with additional quantities of tin and acid although the author preferred to reject all insoluble fractions formed at first or during subsequent removal of the tin with hydrogen sulfide. The α,β-dipyridyl was often recovered from the insoluble precipitates by adding alkali and extracting with ether and used for later reductions. When free from tin the hydrochloric acid solution turned wine-red on evaporation. The addition of caustic potash produced an orange-red color and liberated the base, which was extracted with ether containing alcohol. The extract was evaporated and the residue distilled under reduced pressure. The distillate was dissolved in ether, and the reduced product was washed out with a small quantity of water. The reduced product was recovered by adding alkali and extracting with ether–alcohol, followed by evaporation of the solvent and distillation. The product thus obtained should be either neonicotine or isoneonicotine. Results show that the product obtained by the tin reduction of α,β-dipyridyl is probably isoneonicotine and is α-pyridyl-β-piperidine.

Isoneonicotine picrate melted at 217–218° (corr.); neonicotine picrate melted at 212–213°. A mixture of the two melted at 200°. When isoneonicotine was oxidized with potassium permanganate, the only acid produced was picolinic acid. Neonicotine was at first readily oxidized by permanganate but then seemed to resist further oxidation so that the expected nicotinic acid was not found. The permanganate oxidation of neonicotine and its alkyl derivatives will be studied further.

Isoneonicotine boils at 282° (760 mm) with partial decomposition. Its odor is similar to that of neonicotine.

α,α-Pyridyl-piperidyl.—α,α-Dipyridyl was reduced with tin and hydrochloric acid, four parts of tin to one of dipyridyl. Heat was applied toward the end of the reaction to dissolve the tin completely. Considerable insoluble double chloride of tin and unreduced dipyridyl was formed and removed by filtration. Filtration was also used to eliminate it when it was formed during the removal of the hydrochloric acid by evaporation and of the tin with hydrogen sulfide. When free from tin, the acid solution of the α,α-pyridylpiperidine turns green on evaporation. Addition of alkali turns the solution purple and liberates the base, which was extracted by ether. The base, after removal of the ether, was distilled under reduced pressure. It still contains some α,α-dipyridyl and other contaminating oil, which can be removed by petroleum ether extraction of the aqueous solution. The free base finally obtained has a sperm-like odor similar to neonicotine. It boiled at 265–266° (756 mm.).

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.07; H, 8.64. Found: C, 73.97; H, 8.71.

α,α-Pipyridylpiperidine forms a picrate melting at 187°, crystallizing from water in small prisms. The nitroso derivative was formed as an insoluble oil. After extraction by ether and evaporation of the solvent it remained an oil and was not further studied.

Isonicotine (**γ-Pyridyl-γ-piperidine**).—Isonicotine was first prepared by Weidel and Russo. The author prepared several lots of 30 g. each by hydrochloric acid reduction of γ,γ-dipyridyl, rejecting all insoluble double chlorides formed during the isolation of the base. The reduction of γ,γ-dipyridyl by this method appears to be more readily effected than the reduction of any of the other dipyridyls tried.

Isonicotine was obtained as a pleasant smelling substance quite different in odor from the other pyridylpiperidines studied, which have more of a sperm- and nicotine-like odor. It distilled water white in a partial vacuum, solidifying to a hard mass of crystals melting at about 80° as described by Weidel and Russo. After several distillations in a partial vacuum to remove all water, isonicotine begins to boil at 292° under atmospheric pressure. The thermometer slowly rises during the distillation because of polymerization, and a residue is left in the flask. Evidently 292" is the proper boiling point (Weidel and Russo gave it as far above 260°). Isonicotine forms a picrate, crystallizing from water in prismatic needles which melt at 215–218° with evolution of gas.

When treated in concentrated solutions with sodium nitrite and dilute hydrochloric acid, the nitroso derivative separated as an oil, which was extracted with ether. The evaporation of the ether leaves the nitroso derivative, which crystallizes. After reaystallization from dilute alcohol it was found to melt at 112°.

The methylation of isonicotine by means of dimethyl sulfate, methyl iodide or potassium methyl sulfate always resulted in complete failure. The first two reagents caused the formation of nothing but tar even when the reaction was very carefully moderated. The potassium methyl sulfate did not react at all.

Nicotidine.[8]—The reduction of β,β-dipyridyl with tin and hydrochloric acid was found to be very incomplete. More than 80% of the dipyridyl was recovered as the hydrochloride after the removal of the tin and the addition of absolute alcohol. β,β-Dipyridyl seems to resist reduction more than any of the other dipyridyls tried (α,γ not available).

The reduction of β,β-dipyridyl with sodium and absolute alcohol was also tried. Eight grams of dipyridyl dissolved in 300 cc. of absolute alcohol was reduced with 15 g. of sodium. Examination of the reduced base showed considerable unaltered dipyridyl along with nicotidine. Treatment with absolute alcohol and hydrochloric acid was used to remove dipyridyl and dipiperidyl. The nicotidine distilled at 284–285° and is a viscous oil with an odor similar to that of neonicotine. The product was not pure, as shown by the character of the picrate first formed. Several recrystallizations were required to obtain a product melting at about 206°.

β-Pyridyl-γ-piperidine.—β,γ-Dipyridyl seems to be more readily reduced than α,α-, β,β- or α,β-dipyridyl but less readily than γ,γ-dipyridyl. The usual insoluble double salt did not appear until the acid was evaporated to low volume and the residue diluted with water. The combined insoluble precipitates contained about 30% of the original dipyridyl. The reduced oil fraction was shown still to be impure by the appearance and melting point of the picrate obtained after precipitation in alcoholic solution and recrystallization from water. The picrate consisted largely of leaflets mixed with needles and melted around 233° after darkening around 210°. The product was finally purified through the nitroso derivative, which separated as an oil and was extracted with ether. After decomposition with concentrated hydrochloric acid, liberation of the base with alkali, and distillation under reduced pressure, the resulting oil formed a picrate in long fern-like needles. The recrystallized product melted with slight darkening at 240° and appeared to be a uniform product.

The reduction product of this dipyridyl proved to be β-pyridyl-γ-piperidine because it gave only nicotine acid on oxidation with potassium permanganate.

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[8] Skraup and Vortmann, *Monatsh.*, 4, 597 (1883).

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.07; H, 8.64. Found: C, 73.87, 74.20; H, 8.67, 8.82.

Summary

1. Neonicotine (β-pyridyl-α-piperidine) was separated from the products obtained in the author's sodium–pyridine–oxygen reaction. Nicotimine, isolated by Pictet and Rotschky from the nicotine alkaloids and tentatively identified by them as the same product, is probably different.

2. The reduction of γ,γ-, β,γ-, α,α- and β,β-dipyridyls by tin and hydrochloric acid results in varying yields of the corresponding pyridylpiperidines. The ease of reduction is probably greatest with γ,γ, diminishing in the order given, β,β being the least easily reduced.

3. Attempted synthesis of neonicotine from α,β-dipyridyl usually resulted in isoneonicotine but further study is to be made to accomplish this end successfully.

WASHINGTON, D. C.

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

THE α,α'-DIMETHYLSUBERIC AND α,α'-DIBROMO-α,α'-DIMETHYLSUBERIC ACIDS

BY CATHERINE CASSELS STEELE[1]

RECEIVED OCTOBER 27, 1930 PUBLISHED JANUARY 12, 1931

Satisfactory methods for the preparation of tetramethylene bromide (1,4-dibromobutane) have not been available until recent years, with the result that, although several α,α'-dialkyl substituted adipic[2] and pimelic[3] acids have been synthesized, the corresponding derivatives of suberic acid (1,6-hexane-dicarboxylic acid) are unknown. Perkin[4] used a crude mixture of tetra- and pentamethylene bromides on the sodium salt of malonic ester, but obtained from the action of the tetramethylene bromide only the closed chain compound, ethyl 1,1-pentamethylene-dicarboxylate. In the preparation of the dialkyl acids, one molecular proportion of the bromide was condensed with one of the sodium salt of malonic ester to give two products; one was the ester of a closed chain acid[5] and the other the ester of a straight chain tetracarboxylic acid.[6] The latter results from the action of one mole of bromide on two moles of malonic ester.

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[1] Commonwealth Fund Fellow.

[2] Lean, J. Chem. *Soc.*, 65, 1004 (1894).

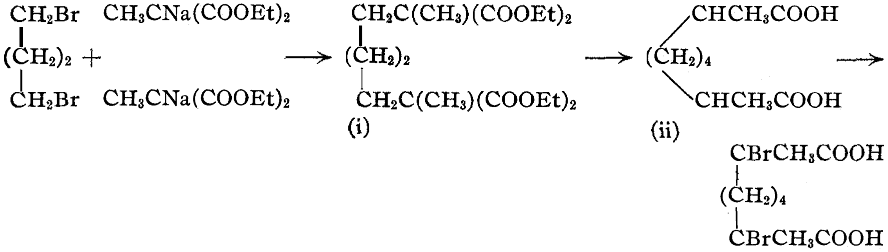
[3] Perkin and Prentice, *ibid.*, 59, 829 (1891).

[4] Perkin and Haworth, *ibid.*, 65, 88 (1894).

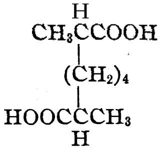
[5] Ethyl trimethylene-dicarboxylate, Perkin, *ibid.*, 47, 807 (1885); ethyl tetramethylene-dicarboxylate, Perkin, *ibid.*, 51, 2 (1887).

[6] Ethyl butane-tetracarboxylate, Perkin, *ibid.*, 51, 19 (1887); ethyl pentane-tetracarboxylate, Perkin, *ibid.*, 51, 241 (1887); Curtius, *J. prakt. Chem.*, [2] 94, 340 (1916).

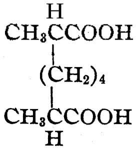
The esters of the straight chain tetracarboxylic acids were then alkylated in the α,α'-positions by treating the disodium salt with an alkyl bromide.[3] Hydrolysis of this product and heating to split off carbon dioxide gave the α,α'-substituted dibasic acids.[2,3] A simpler method was used by Perkin[7] in the preparation of α,α'-di-isobutylpimelic acid, in which he condensed trimethylene bromide with 2 moles of isobutylmalonic diethyl ester. The only other use made of this method in such syntheses was in the preparation of α,α'-dimethyladipic acid from ethylene bromide and monomethylmalonic diethyl ester.[8]



In the present investigation one molecular proportion of tetramethylene bromide was condensed with two of sodiomethylmalonic diethyl ester to give ethyl dimethylhexane-tetracarboxylate (i) in 40% yield. Hydrolysis of the ester gave the tetracarboxylic acid and on heating the latter to 240° α,α'-dimethylsuberic acid (ii) was obtained. This acid was found to exist in two isomeric forms, with melting points of 132–133° and 91–92°, respectively. One of these must be a racemic mixture (dl), and the other an internally compensated (or *meso*) form.



(*dl*)



(*meso*)

No attempt has yet been made to distinguish between the two forms.

The α,α'-disubstituted adipic acids exist in two forms;[2] of the corresponding pimelic series[9] only α,α'-dimethoxypimelic acid has been separated, by crystallization of the amide.[10] α,α'-Dibromosuberic acid,[11] prepared by the bromination of suberic acid, and α,α'-dimethoxysuberic acid[11] both exist in two forms, and α,α'-dimethoxyazelaic acid[11] was separated through the amides.

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[7] Perkin, J. Chem. *Soc.*, 59, 819 (1891).

[8] Kitzing, *Ber.*, 27, 1578 (1894).

[9] Perkin and Prentice, J. *Chem. Soc.*, 59, 820 (1891).

[10] Hassell and Ingold, *ibid.*, 129, 1470 (1926).

[11] Goss and Ingold, *ibid.*, 129, 1473 (1926).

The fact that a dialkyl suberic acid also exists in two forms seems to indicate that the abnormality in the pimelic series is due to mechanical difficulty in separating the two isomers, and not to the existence of only one form of alkyl derivative, although it is surprising that six dialkyl derivatives, and the dibenzyl, dibenzal and dibromopimelic acids were all isolated as single compounds.

Bromination of α,α'-dimethylsuberic acid should result in an α,α'-dibromo-α,α'-dimethylsuberic acid. Treatment with red phosphorus and bromine, a method used successfully on suberic acid by Hell and Gantter,[12] surprisingly did not give the expected compound, but a mixture of partially brominated products, some of which were unsaturated. The dibromide, however, was obtained by the action of bromine on the acid chloride, as in the bromination of suberic acid by Ingold.[11]

Both forms of α,α'-dimethylsuberic acid gave as the main product a dibromo acid, m. p. 200–210° *ex* ethyl acetate and although in both cases the crude mixture melted about 185°, a distinct crystalline second form was not obtained.

The original goal of this investigation was the preparation of *cis*-1,2-dimethylcyclohexane-1,2-dicarboxylic anhydride. This compound ought to be identical with deoxycantharidin, which is obtained from the naturally occurring drug cantharidin by the action of hydrogen bromide and subsequent reduction of this "dibromide" with zinc and acetic acid.[13] Coffey[14] prepared *cis*-cyclohexane-1,2-diacetic anhydride and *cis*-1,2-dimethylcyclohexane-4,5-dicarboxylic anhydride, these being the structures for deoxycantharidin derived from the other two possible formulas assigned to cantharidin. He found neither of these identical with the deoxycantharidin derived from the natural product but recorded no synthesis of the 1,2-dicarboxylic anhydride. In this work it was hoped to obtain it from dibromodimethylsuberic acid by the elimination of bromine and consequent formation of a cyclohexane ring, but treatment of both the bromo acid and its dimethyl ester with copper bronze or molecular silver met with no success.

Experimental Part

Preparation of Tetramethylene Bromide.—The simplest method recorded in the literature is that of Müller,[15] who passed hydrogen bromide into tetramethylene glycol at 80°, using Böeseken's[16] preparation of the latter by the reduction of diethyl succinate with sodium and alcohol. The glycol has been made in this Laboratory according to this method, with the modification that, after removal of the alcohol and toluene by distillation in steam, the residue was extracted continuously for forty-eight hours with

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[12] Gantter and Hell, *Ber.*, 15, 147 (1882).

[13] Gadamer, *Arch. Pharm.*, 252, 636 (1914); Rudolph, *ibid.*, 254, 423 (1916).

[14] Coffey, *Rec. trav. chim.*, *42*, 387, 1026 (1923).

[15] Miiller, *Monatsh.*, 49, 27–30 (1928).

[16] Boeseken, *Rec. trav. chim.*, *34*, 100 (1915).

ether and the glycol distilled, b. p. 148° (30 mm.). The bromination was carried out in a manner analogous to the preparation of trimethylene bromide[17] except that the mixture was refluxed for eight hours instead of three. A 70% yield of distilled bromide was obtained, b. p. 106–110° (30 mm.)

Monomethylmalonic Diethyl Ester.—The action of either methyl iodide[18] or methyl bromide[19] on sodio-malonic ester gives a product which one cannot say with certainty is not contaminated with malonic or dimethylmalonic ester. Zane and Ingold[20] purified the product by hydrolysis, crystallization of the acid, and re-esterscation. The method employed in this work was to convert ethyl a-bromopropionate to ethyl α-cyanopropionate, and to hydrolyze the nitrile. Zelinsky[21] treated ethyl a-bromopropionate in absolute alcohol with potassium cyanide, heated and agitated the mixture with hot air for six hours and obtained a yield of 18% a-cyano ester; the main product of the reaction was dimethylcyanosuccinic ester. It was found by making a series of runs, using a steam-bath and a mechanical stirrer, that an optimum time existed for the yield of ethyl a-eyanopropionate and a correspondingly small amount of the succinic ester; the yield, based on the amount of a-bromo ester actually used in the reaction, was obtained as high as 43%.

To a boiling suspension of 144 g. of potassium cyanide in 195 g. of absolute alcohol was added, as rapidly as possible, 387 g. of ethyl α-bromopropionate (b. p. 158°), the mixture being mechanically stirred after about one-third of the ester had been added. Boiling was then continued for nine and a half hours, the mixture was cooled, filtered and the filtrate and washings poured into 2 liters of water. The oily product was washed and distilled under atmospheric pressure with the use of a 25–30 cm. fractionating column, when the following fractions were obtained

155–170°	Unreacted a-bromo ester	154 g.
170–185°	Intermediate fraction	10 g.
195–205°	Ethyl a-cyanopropionate	70.5 g.

A second distillation of the cyano ester gave a boiling range of 197–198°, the residue being succinic ester.

Hydrolysis and esterification of the nitrile were accomplished in one operation.[22] A cold, thoroughly agitated solution of 127 g. of ethyl α-cyanopropionate in 196 g. of 95% ethyl alcohol was treated gradually with 196 g. of concd. sulfuric acid, then gently refluxed for seven hours, cooled and poured into 2 liters of water. The oily layer was washed with dilute sodium carbonate solution, and on distillation gave 118 g. (93%), b. p. 104–105° (27 mm.).

Ethyl **Dimethylhexane-tetracarboxylate.**—23.8 g. of metallic sodium was added to a solution of 180.5 g. of monomethylmalonic diethyl ester in 1 liter of absolute alcohol (magnesium dried) contained in a 3-liter, 3-necked flask fitted with a mechanical stirrer, condenser and dropping funnel. The mixture was warmed until a clear solution was obtained,[23] then treated with 112 g. of tetramethylene bromide, and refluxed for eighteen

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[17] Kamm and Marvel, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 8.

[18] Conrad, Ann., 204, 134 (1889).

[19] Lucas and Young, THIS JOURNAL, 51, 2536 (1929).

[20] Zane and Ingold, *J. Chem. Soc.*, 129, 14 (1926).

[21] Zelinsky, *Ber.*, 21, 3162 (1888).

[22] Compare conversion of benzoyl cyanide to ethyl phenyl acetate, Adams and Thal, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1922, Vol. II, p. 27.

[23] The sodium salt of methylmalonic diethyl ester is practically insoluble in toluene, so the use of this solvent, which was tried first, was discontinued.

hours. The alcoholic solution, decanted from the sodium bromide, and the washings were distilled to remove most of the alcohol; the residue, poured into water, gave an oil which, after being washed with water, was separated into the following fractions by distillation

90–125° (30 mm.)	35 g. water and unchanged ester
150–160° (6 mm.)	61.5 g. (a)
210–217" (6 mm.)	83 g. (b)

(a) is 3-butenyl monomethylmalonic diethyl ester,[24] and (b) is the required dimethylhexane-tetracarboxylate (40% yield).

Anal. Calcd. for $C_{20}H_{34}O_8$: C, 59.7; H, 8.45. Found: C, 59.53; H, 8.37.

Dimethylhexane-tetracarboxylic Acid and α,α'-Dimethylsuberic Acid.—Eighty-two grams of the ester [(b) above] was hydrolyzed by boiling with 90 g. of potassium hydroxide in 1 liter of 95% alcohol for fifteen hours with mechanical stirring. The solution, diluted with water, was taken to dryness in an evaporating dish, the residue taken up in the minimum amount of water, and refluxed for four hours with 180 cc. of concd. hydrochloric acid. Dilution with water and evaporation to dryness gave a mixture of potassium chloride and the tetrabasic acid, 58 g. (calcd. 60 g.) of the latter being isolated by five extractions with ether. It was not purified further, but heated in a metal-bath at 240° for twenty minutes (or until all the carbon dioxide was expelled), giving 38 g. (calcd. 41 g.) of crude dibasic acid.

The Two Isomeric Forms of Dimethylsuberic Acid.—The following method of separating the isomers was adopted. The dibasic acid was extracted five times with boiling water, the aqueous solutions decanted off the dark, oily material, and filtered hot through ordinary filter paper. The first fractions which separated had melting points in the range 100–118° (18 g. from 38 g. of crude) and these on five recrystallizations from boiling water gave small, colorless plates with constant m. p. 132–133° (first form). Second fractions from the original extracts gave similarly an additional 1 g.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.4; H, 8.91. Found: C, 59.34; H, 8.79.

The other isomer was isolated from the fractions melting below 100" by first washing out oily material with cold ligroin, then dissolving in boiling ligroin and filtering from any insoluble material. The solution on cooling deposited crystals which on two recrystallizations gave 3.5 g. of small, glistening prisms, m. p. 91–92" (second form).

Anal. Calcd. for $C_{10}H_{18}O_4$: neut. equiv., 101. Found: 102.4.

Dimethylsuberic Diethyl Ester.—Forty grams of the crude acid was esterified in the usual manner; 43 g. of the diethyl ester was obtained (84%), b. p. 178–185° (25 mm.).

Bromination of α,α'-Dimethylsuberic Acid, First Form.—(a) An intimate mixture of 5 g. of acid (m. p. 132–133°) and 0.5 g. of red phosphorus was allowed to stand overnight with 6 cc. of bromine, then warmed gently and air blown through to remove excess bromine. On addition of water and warming to decompose the acid halide, partial carbonization took place and no pure compound was isolated.

(b) Eleven grams of the acid, 1.2 g. of red phosphorus and 12 cc. of bromine were allowed to stand overnight, then treated slowly with methyl alcohol; the solution was poured into a large volume of water, and extracted with ether. On distillation, the following fractions were obtained

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[24] Compare the allyl compounds obtained by Kipping and Perkin, *J. Chem. Soc.*, 57, 32 (1890), and Perkia, *ibid.*, 59, 819 (1891).

(i) 4 2 g. 156–160° (30 mm.) *Anal.* Found by Stepanov method: Br, 12.87
(ii) 4.3 g. 175–185° (30 mm.) *Anal.* Found by Stepanov method: Br, 24.88
(iii) 1.3 g. 180–188° (12 mm.) (Copious evolution of fumes)

Calcd. for $C_{12}H_{20}O_4Br_2$: dibromo acid: Br, 41.18
Calcd. for $C_{12}H_{21}O_4Br$: monobromo saturated acid: Br, 25.24
Calcd. for $C_{12}H_{19}O_4Br$: monobromo unsaturated acid: Br, 26.05

(i) and (ii) did not decolorize permanganate immediately, but were oxidized by it on standing. (iii) decolorized permanganate immediately.

(c) **α,α'-Dibromo-α,α'-dimethylsuberic Dimethyl Ester.**—Thirteen grams of the acid of m. p. 132–133° was warmed with 11.2 cc. of thionyl chloride in a flask fitted with a ground-in water condenser until there was no further reaction; 10.4 cc. of bromine was then added gradually, the mixture kept hot on the steam-bath for eight hours, then cooled and treated with absolute methyl alcohol. On distillation 19.5 g. of ester was obtained (78%), b. p. 216–219° (30 mm.). It was colorless when freshly distilled, but turned brown on exposure to air.

(d) **α,α'-Dibromo-α,α'-dimethylsuberic Acid.**—Three grams of acid of m. p. 132–133° was treated as above with thionyl chloride and bromine. After standing overnight it was warmed with about 50 cc. of water until all the sirup had decomposed to a hard, crystalline mass. This was filtered off and washed with water: yield, 3.8 g., m. p. 177–193° with decomposition.

Anal. Calcd. for $C_{10}H_{16}O_4Br_2$: Br, 44.4. Found for crude acid: Br, 46.9.

On two recrystallizations from ethyl acetate the acid had the constant m. p. 200–201°. The original mother liquor, when taken to dryness, gave 1 *g.* of partially crystalline material which could not be recrystallized from any of the ordinary solvents.

Second Form. Bromination of Second Form of Dimethylsuberic Acid.—Two and one-half grams (m. p. 91–92°) was brominated in the manner outlined above. The crude product consisted of 3.9 g. of m. p. 194–196°, and on recrystallization from ethyl acetate 2 g. was obtained, m. p. 200–201"; this gave a mixed melting point with the acid melting at 200–201° from (d) of 200–201°. The initial mother liquors gave 1.2 g. of sirupy material on evaporation to dryness.

Anal. Calcd. for $C_{10}H_{16}O_4Br_2$: Br, 44.4. Found for pure acid: Br, 44.4.

Attempts at **Ring Closure.**—(a) A mixture of 10 g of copper bronze and 18.6 g. of ester on heating to 140° appeared to boil suddenly and evolved copious fumes. When the mass was cooled, extracted with alcohol and distilled, only low-boiling fractions were obtained and no definite compound was isolated

(b) When a suspension of copper bronze in a solution of 2 g. of the acid in nitrobenzene was heated to 160°, the liquid darkened and the copper lost its luster. Heating was continued at this temperature for an hour, with addition of more copper at intervals, the mixture cooled, filtered and most of the solvent removed by distillation. Precipitation from the residue with petroleum ether (b. p. 40–60°) gave a sirupy product which could not be induced to crystallize.

(c) A solution of 2 g. of the acid in 35 cc. of acetone was shaken for twenty-four hours with 1.6 g. of molecular silver, then filtered and the filtrate taken to dryness. On one recrystallization from ethyl acetate, the material had the melting point 200–201°, gave a positive test for bromine, and a mixed melting point with the starting material (m. p. 200–201°) was exactly the same.

The author wishes to record her indebtedness and thanks to Professor Roger Adams, at whose suggestion this work was undertaken, and with whose help and criticism it was carried out.

Summary

1. Tetramethylene bromide was prepared by the action of a solution of hydrobromic acid and sulfuric acid on tetramethylene glycol. Monomethylmalonic diethyl ester was prepared from ethyl a-cyanopropionate, and the conditions for the maximum yield of the latter product from α-bromopropionate were elaborated.

2. Methylmalonic ester and tetramethylene bromide were condensed to give ethyl dimethylhexane-tetracarboxylate, which on hydrolysis and decomposition at 240° gave α,α'-dimethylsuberic acid.

3. α,α'-Dimethylsuberic acid exists in two isomeric forms, both of which were isolated pure. Bromination of either acid gave as the principal product one and the same α,α'-dibromo-α,α'-dimethylsuberic acid.

4. Attempts to form a cyclohexane ring by removal of bromine with copper bronze and molecular silver were unsuccessful.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

SYNTHESIS AND PYROLYSIS OF METHYLALLENE AND ETHYLACETYLENE[1]

BY CHARLES D. HURD[2] AND RICHARD N. MEINERT[3]

RECEIVED NOVEMBER 3, 1930 PUBLISHED JANUARY 12, 1931

The only previous mention of methylallene in the literature is its synthesis in 1888 by Norton and Noyes.[4] They listed its boiling point at 19° and prepared its tetrabromide. The synthesis was effected through "butyric chloral" by the following steps

$$CH_3—CHCl—CCl_2—CHO \xrightarrow{Zn(C_2H_5)_2} CH_3CHClCCl_2CH_2OH \xrightarrow{PCl_5}$$

$$CH_3CHClCCl_2CH_2Cl \xrightarrow{Zn \times Cu} CH_3—CH{=}C{=}CH_2$$

Since that time a few general methods of synthesis for allenes have been developed, none of which, however, has received application in the synthesis of methylallene. Bouis' general method[5] seemed to possess definite advantages and was therefore selected.

Crotonaldehyde was the starting point in the synthesis. It was reduced

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[1] This paper contains results obtained in an investigation on "The Pyrolysis of Pure Hydrocarbons" listed as Project No. 18 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.

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[4] Norton and Noyes, *Am.* Chem. *J.*, 10, 430 (1888).

[5] Bouis, Compt. rend., 182, 788 (1926); 183, **133** (1926).

to crotyl alcohol, which, in turn, was changed into crotyl bromide. On bromination the latter yielded 1,2,3-tribromobutane. Treatment of this with potassium hydroxide gave rise to 2,3-dibromo-1-butene which, on treatment with zinc dust suspended in ethyl alcohol, yielded methylallene. The steps in this synthesis are

$$CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCH_2OH \longrightarrow CH_3CH{=}CHCH_2Br \longrightarrow$$
$$CH_3CHBrCHBrCH_2Br \longrightarrow CH_3CHBrCBr{=}CH_2 \longrightarrow CH_3{-}CH{=}C{=}CH_2$$

The boiling point of methylallene was found to be 10.3° instead of 19" as was reported by Norton and Noyes. This boiling point was obtained with a standardized thermometer, using a vacuum-jacketed spiral column having a cooling cup at the top of the column so that a drip-back could be maintained. From this, it seems that the older value is in error, possibly due to superheating of the vapor. Other physical constants of methylallene were also determined, as no values for the density or the refractive index have been previously recorded.

No mention of 2,3-dibromo-1-butene is made in the literature. For this reason it was studied in some detail. Methylallene tetrabromide was mentioned in Norton and Noyes' paper but none of its properties was listed. Therefore, it was synthesized, analyzed and its physical properties determined. It was prepared both by bromination of methylallene and by bromination of 2,3-dibromo-1-butene.

Comparison of the Pyrolysis of Allene and **Methylallene.**—It was found that methylallene resembles allene in its mode of pyrolysis. At temperatures from 500 to 550°, a complete decomposition was effected in thirty-six seconds and three-fourths of the methylallene was converted into liquids of a polymeric nature. Some tarry material and a little carbon were deposited on the walls of the reaction tube.

The liquids were separated as efficiently as possible into fractions containing but one polymer. The lowest boiling fraction was obtained in a state of fairly high purity. It boiled at 110–115° and a molecular weight determination showed that it was a dimer of methylallene. Attempts to prove its structure by permanganate oxidation or by ozonization were not fruitful.

Inasmuch as allene was found[6] to pyrolyze 66 and 81% in fifty-five and eighty-six seconds, it is evident that it is more resistant to heat than methylallene which was almost completely altered in thirty-six seconds. Although the gaseous products from both allene and methylallene were the lesser products of the reaction, it is interesting to note that methylallene, even with its considerably shorter contact time, gave more than twice the volume of gaseous products. As compared with 77–132 cc. of gas from each liter of allene pyrolyzed, methylallene gave rise to 235–308 cc. Evidently the methyl group is the responsible factor, for much of the

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[6] Meinert and Hurd, THIS JOURNAL, 52, 4540 (1930).

increased volume was due to methane. Paraffin hydrocarbons made up about half of the total volume of the gases, and the n in C_nH_{2n+2} was considerably nearer unity in the gases from methylallene.

There is another interesting difference between allene and its homolog. Whereas the former is isomeric with only one member of the acetylene series, methylallene is isomeric with two, namely with ethylacetylene and dimethylacetylene. In addition, butadiene-1,3 is also isomeric. Of these three, ethylacetylene would be analyzed with acetylene as "acetylenes" with the alkaline potassium iodomercurate reagent. Dimethylacetylene and butadiene would be taken up in the 82.5% sulfuric acid pipet, if not in the 62.5% pipet. Such a mixture of propylene, allene, butadiene and dimethylacetylene would defy identification with the present methods of analysis, but since the total quantity of these gases was small it is evident that such transformations, even if present, must be very minor effects.

Ethylacetylene.—Ethylacetylene has been prepared by several workers, but there is no record of its pyrolysis. Both Reboul's and Lespieau's methods[7] of preparation are open to the criticism that the ethylacetylene might be contaminated with methylallene. In the former method hydrogen bromide is detached from 2-bromo-1-butene by alcoholic potassium hydroxide. In the latter method, two moles of hydrogen bromide are detached from 1,2-dibromobutane. Picon's method,[8] wherein ethyl iodide is made to react with sodium acetylide in liquid ammonia, is not open to this objection. Therefore this method, or rather a modification of it, was used in the present study. It was found that diethyl sulfate could be substituted for the much more expensive ethyl iodide. Both methods were tried and it was found that the reaction proceeded more smoothly when the sulfate was used than when the iodide was employed. The equation is

$$NaC{\equiv}CH + (C_2H_5)_2SO_4 \longrightarrow C_2H_5C{\equiv}CH + Na(C_2H_5)SO_4$$

A similar synthesis of methylacetylene, using sodium acetylide and dimethyl sulfate, has been described recently.[6] There is every reason to believe that this reaction with alkyl sulfates is general. No doubt alkyl *p*-toluenesulfonates could also be used with success.

The boiling point of the ethylacetylene, made by the diethyl sulfate procedure, was 8.5°. This is in agreement with Picon, who also reported 8.5°, but contradicts the work of Reboul, who reported 14–14.5°, and also contradicts the work of Lespieau, who reported 18°.

The relationship between allene and methylacetylene has been shown previously[e] to be a predictable one on the basis of the three-carbon system inasmuch as methylacetylene pyrolyzed into allene. In the present study we were interested to see if ethylacetylene and methylallene bore a

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[7] Reboul, *Compt. rend..* 113, 591 (1891); Lespieau, *Ann. chim.,* [8] *27,* 146 (1912).

[8] Picon, *Compt. rend., 158,* 1184 (1914).

similar relationship, in which case an equation to represent it would be: $CH_3CH_2C{\equiv}CH \longrightarrow CH_3CH{=}C{=}CH_2$. The reverse change, that of methylallene into ethylacetylene, has been brought about[9] by heating with sodium,

When ethylacetylene was pyrolyzed, it was found that liquids were not so abundantly formed as was the case with methylacetylene. At 580 and 600° only one-third of the gas pyrolyzed appeared as liquids. Comparatively large amounts of gaseous products were formed. Thus, at 600° there were formed from each liter of ethylacetylene pyrolyzed the following amounts of gases: 94 cc. of acetylenes, of which less than a fifth was methylacetylene; 70 cc. of propylene, with possibly a small admixture of allene; 108 cc. of ethylene; 170 cc. of hydrogen, and 435 cc. of paraffins, practically all of which was methane. This total volume of 883 cc. of gas is a little more than double the volume obtained when a temperature of 550° was employed. However, the 403 cc. in the latter case is considerably in excess of the 308 cc. which was produced from ethylallene under almost duplicate conditions. Ethylacetylene was quite stable at 500° using a contact time of thirty-five seconds. Only 23% of it underwent pyrolysis. However, the pyrolysis was practically 100% at 580°.

The liquids obtained were separated into fractions with difficulty, owing to the small amount available. They were shown to be not aromatic in type. Their resemblance to the liquids obtained from the allenes and from methylacetylene was striking, but no definite polymers were identified. Although the refractive index data were of the same order of magnitude as the data from the corresponding fractions obtained from methylallene, the agreement was not close enough to warrant a claim that the two liquids were identical. Certainly, however, they were similar.

Experimental Part

Crotonaldehyde was reduced to crotyl alcohol with ethoxymagnesium chloride using the method of Meerwein.[10] This was converted in 68% yield into crotyl bromide[11] by interaction with 48% hydrobromic acid.

1,2,3-Tribromobutane.—Bromine (80 cc., dried with concd. sulfuric acid) was slowly dropped into a cold and rapidly-stirred solution of 203 g. of crotyl bromide in 300 cc. of carbon tetrachloride. The details for this preparation of tribromobutane were analogous to those for the preparation of 1,2,3-tribromopropane (by adding bromine to allyl bromide) which are given in "Organic Syntheses."[12] The tribromobutane thus produced was twice distilled at 14 mm. The yield was 95% of the theoretical. At 14 mm. it boiled at 100–101° and at 20° its index of refraction was 1.5680. Charon[13]

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[9] Jocicz, J. Russ. *Phys.-Chem. Soc.*, *29*, 90 (1897).

[10] Meerwein, *Ann.*, 444, 221 (1925).

[11] Charon, *Ann. chim.*, [7] *17*, 233 (1899).

[12] Johnson and McEwen, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 99.

[13] Charon, Ref. 11, p. 239.

reported the b. p. to be 113–114° at 21 mm. Delaby[14] reported the b. p. at 19 mm. to be 110–113" and the index of refraction, n_{D}^{15} 1.569.

2,3-Dibromo-1-butene.—In a one-liter balloon flask were placed 419 g. of 1,2,3-tribromobutane, 20 cc. of water and 100 g. of sodium hydroxide. The flask was connected to an efficient condenser by a wide bent tube and a receiving flask was fitted to the condenser by means of an adapter. The receiver was immersed in a bath of ice water. The contents of the flask were heated directly with a small, slightly luminous flame which was directed by the hand against the flask with a rotary motion. The flask was shaken from time to time, and gradually the alkaline layer became emulsified as the reaction progressed. The reaction proceeded very rapidly at first and developed considerable heat, enough in fact to cause spontaneous distillation of some of the product. After the first rapid reaction had subsided, the flask was again heated until all the liquid had distilled over, after which the solid material in the flask was strongly heated until no more distillate was obtained. The bromide in the receiving flask was washed with water, and the bromide layer separated from the water layer. The 2,3-dibromo-1-butene, which contained some unchanged tribromobutane, was then distilled under reduced pressure. The fraction boiling in the range of 85–90° at 40 mm. was collected. The residue, consisting of unchanged tribromobutane, was saved to be worked up with sodium hydroxide after a sufficient amount had accumulated from several runs. The fraction consisting of the dibromobutene with a small amount of the tribromobutane was redistilled; b. p. 75° at 20 mm. The small amount of residue was combined with the previous residues. The yield was 86%. Analyses of the dibromobutene and of the methylallene tetrabromide which follows were performed by Mr. Forrest Pilgrim.

Anal. Subs., 0.2212: AgBr, 0.3875. Calcd. for $C_4H_6Br_2$: Br, 74.72. Found: Br, 74.55.

The physical constants were found to be as follows: density, d_4^{20} 1.8881, index of refraction, $n_{\mathrm{D}}^{2.8}$ 1.5556; n_{D}^{20} 1.5464; $n_{\mathrm{D}}^{26.5}$ 1.5430. The change of the index of refraction with change of temperature, $dn_{\mathrm{D}}/dT = -0.00053$; at 20 mm., the boiling point was 75".

Preparation of Methylallene Tetrabromide.—Fifty grams of 2,3-dibromo-1-butene was added to an equal volume of dry carbon tetrachloride, and the calculated amount of bromide was added slowly. The reaction was slow in starting. As a matter of fact it was necessary to warm the flask gently to start the reaction but after once started it became so exothermic that it was necessary to cool the reacting mixture. When all of the bromine had been added, the solvent was removed and the methylallene tetrabromide was distilled at reduced pressure. The distillate was redistilled, only the middle portion being retained for the determination of the constants.

Anal. Subs., 0.2218: AgBr, 0.4463. Calcd. for $C_4H_6Br_4$: Br, 85.53. Found: Br, 85.63.

The physical constants were found to be as follows: melting point, −2°; b. p. at 7 mm., 97.5"; specific gravity, d_4^{20}, 2.510 (the average of 2.5097 and 2.5103); index of refraction at 3.6°, 1.6152 and at 20.0". 1.6070. From these data, $dn_{\mathrm{D}}/dT = -0.00050$.

The only previous mention of this compound is in the paper of Norton and Noyes in 1888. Therein it was stated to be prepared from methylallene and bromine, and it was stated not to solidify at −17°. In determining the melting point it was found in the present work that the bromide had to be cooled to −40° until solidification occurred, but with a little of the solid material in contact with the liquid bromide, it could be solidified at −2°, and melted within half a degree of this point.

Preparation of **Methylallene.**—A one-liter, three-necked flask was fitted with a

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[14] Delaby, *Compt. rend.,* 176, 589 (1923). These values are used in "International Critical Tables," Vol. I, p. 186.

reflux condenser inclined at an angle of 45°, a dropping funnel, and a tube reaching nearly to the bottom of the flask, so that an inert gas could be used to flush out the apparatus. A delivery tube leading from the top of the condenser was fitted to a 100-cc. distilling flask which served as a trap and was kept at a temperature of 30° by a water-bath. A spiral condenser and receiver was fitted to the side arm of the trap flask. This condenser-receiver was kept at a temperature of −12° by ice and salt. The receiver was so arranged that the condensed liquid could be blown into a bottle for storage without removing any connections. The main reaction flask was heated with a water-bath.

Ethyl alcohol (300 cc.) and zinc dust (160 g.) were placed in the reaction flask. The 2,3-dibromo-1-butene (131 g.) was added slowly through the dropping funnel, during which time the alcohol in the flask was kept boiling vigorously. The methylallene all passed over into the condenser and was liquefied. There was a small amount of alcohol which collected in the trap. The reflux condenser was kept at 35–40° in order to retain the alcohol but at the same time to permit the methylallene to escape. After all of the bromide had been added, the alcohol in the flask was boiled for several minutes and carbon dioxide was bubbled through to sweep out all of the methylallene. The crude material thus obtained was fractionated, using the spiral column previously described. The yield was 72%, calculated on the basis of the pure, distilled methylallene.

The physical properties of the liquid methylallene were as follows: b. p. 10.3"; d_4^0 0.676; $n_{\mathrm{D}}^{1.3}$ 1.4205.

Pyrolysis

Apparatus.—The apparatus used in the pyrolysis of both methylallene and ethylacetylene was the same as has been described by the authors in a previous paper,[15] except for the manner in which the hydrocarbon was introduced into the system. The liquefied hydrocarbon was placed in a 25-cc. water-jacketed buret. The buret was attached by means of a rubber stopper to a 100-cc. distilling flask immersed in a bath at 35°. This served as a vaporizing chamber, and the gas was then led from the side arm of the distilling flask through the flowmeter and manometer connections into the reaction chamber as previously described. A spiral condenser which was immersed in a bath at −15° served to condense any unchanged methylallene which came off with the exit gases.

The exit gaseous mixture was analyzed by the method of Hurd and Spence.[16] Of supplementary interest, it was found that methylallene resembles propylene very decidedly in its rate of absorption in sulfuric acid solutions. Neither of these gases is appreciably soluble in the 62.5% sulfuric acid solution or in the alkaline potassium iodomercurate reagent. In 82.5% sulfuric acid, methylallene and propylene are absorbed at about the same rate. This rate is about 1.2 times faster than the rate for allene. It is interesting to note that in dilute acetic acid allene is absorbed about three times more rapidly than propylene. With a 2:1 solution of glacial acetic acid and water (in an Orsat pipet), 8.2 cc. of methylallene dissolved in two minutes, whereas only 2.7 cc. of propylene was absorbed. The same ratio held in more dilute solutions. For purposes of analysis of allene–propylene mixtures by this method, a ratio considerably greater than 3:1 would be required.

Pyrolysis of **Methylallene.**—The data obtained in four experiments are given in Table I.

In the first run, the off-gas consisted almost entirely of the carbon dioxide

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[15] Meinert and Hurd, This Journal, 52, 4540 (1930).

[16] Hurd and Spence, *ibid.*, 51, 3356–7 (1929).

TABLE I

RESULTS OF THE PYROLYSIS OF METHYLALLENE

Run number	1	2	3	4
Temperature, °C.	405	500	500	550
Methylallene used, g.	13.1	20 1	20.1	11 2
Methylallene used, cc. as gas	5420	8340	8330	4640
Volume of off-gas, cc.	600	2160	3040	1838
Pressure in tube, mm.	725	720	737	727
Rate of flow of in-gas, cc./min.	132	135	137	129
Contact time, sec.	46.3	36.6	36 1	37.0
Analysis of off-gas, % by vol.				
Carbon dioxide	85	5.2	8.2	17.9
Acetylenes	..	3.3	2.7	0.7
Gas soluble in 62.5% H_2SO_4	..	1.1	1 7	2 5
Gas soluble in 82.5% H_2SO_4	..	19.1	19.0	19 0
Ethylene	..	8.1	8.1	5.7
Hydrogen	..	12.0	13.1	7.5
Paraffins	..	47.1	39.6	43.8
n in C_nH_{2n+2}	..	1.23	1.19	1.33
Percentage of pyrolysis	28	95–100	95–100	95–100
Weight of liquids, g.	3	14.6	14 8	8.0
% of liquids by wt. of methylallene pyrolyzed	22	72 7	73.6	73.2
Total volume of gaseous products formed, cc.				
Acetylenes	..	72	82	13
Soluble in 62.5% H_2SO_4	..	24	52	46
Propylene, allene, etc.	..	410	577	349
Ethylene	..	175	246	105
Hydrogen	..	260	398	138
Paraffins	..	1018	1204	806
Cc. of gases formed per liter of entering methylallene				
Acetylenes	..	8.6	9.9	3.0
Soluble in 62.5% H_2SO_4	..	3.0	6.2	10.0
Propylene, allene, etc.	..	49.2	69.2	75.8
Ethylene	..	21.0	29.5	22.6
Hydrogen	..	31.2	47.8	29 9
Paraffins	..	122.0	145.0	173.4

used to fill the system at the start of the experiment. No analysis of the remainder of this gas was made.

Reference to Table I shows that the reaction leading to the formation of liquids of high boiling point was the major effect in this pyrolysis. This was also the case with allene. The gaseous products were relatively unimportant, with the exception of the paraffin hydrocarbons which were present to the extent of 12–17% of the volume of methylallene pyrolyzed. Some carbon was deposited in the reaction tube.

The liquids which were obtained when methylallene was pyrolyzed were fractionally distilled using a 100-cc. Claisen flask which was equipped with a Vigreux column. The higher-boiling fraction was distilled under reduced pressure. The following fractions were obtained:

Fraction	B. p., °C.	n_D	Weight, g.
A	30–42	....	1.3
B	42–75	....	0.7
C	75–135	1.4815	6.6
D	135–200	1.4978	9.1
E	100-200 (33 mm.)	1.547	8.6
Residue			10.7

The residue was a very viscous, rubbery material that partially solidified on cooling.

Fraction A was shown to contain considerable unchanged methylallene by preparing the bromide. A mixture of the di- and tetrabromides was obtained as is always the case, and this was fractionally distilled in so far as the small volume would permit. The first portion boiled at 120–130° at 40 mm. and had a refractive index of 1.5408 at 26.5'. If pure, 2,3-dibromo-1-butene has a refractive index of 1.5430 at 26.5'. The second portion boiled at 150–160° at 40 mm. and had a refractive index of 1.5905 at 27.5'; $n_D^{27.5}$ for pure methylallene tetrabromide is 1.6033. The first portion was evidently the dibromide and the second was largely the tetrabromide of methylallene, with a small amount of the dibromide as an impurity. No solid tetrabromide was produced, which fact speaks for the absence of butadiene tetrabromide in this material.

Portion C of the liquids was purified by distillation. It was perfectly clear and had an odor resembling that of kerosene. The boiling point was 110–115° and the refractive index 1.4758 at 27°. The molecular weight of this sample was determined by the Victor Meyer method.

Mol. *wt.* Subs., 0.1582, 0.0809: cc. of gas formed, 41.7 at 26°, 752.7 mm.; 18.4 at 29°, 748.3 mm. (measured over water). Mol. wt. found: 97.7, 116. Mean, 105.9. Calculated mol. wt. of C_8H_{12}: 108.

This, together with the boiling point and the refractive index, shows that fraction C is a dimer of methylallene or perhaps a mixture of several dimers, inasmuch as several are possible.

Preparation of Ethylacetylene.—Thirty-six grams of sodium was dissolved in about 500 cc. of liquid ammonia. Then acetylene was passed into the solution till the blue color, characteristic of sodium in liquid ammonia, had disappeared. Following this, 230 g. of diethyl sulfate was added slowly, keeping the flask at −60°. Essentially the apparatus and procedure was identical to the one which has been recently described for the synthesis of methylacetylene[17] from dimethyl sulfate and sodium acetylide. The preparation of ethylacetylene by this method proceeded even more smoothly than the preparation of methylacetylene.

The ethylacetylene was liquefied and fractionally distilled, using a low-pitched, vacuum-jacketed spiral[18] column. It boiled at 8.5°, which is in agreement with the value found by Picon. The yield of the pure, redistilled ethylacetylene was 97.5 g. which represents a yield of 60%, based on the equation $Et_2SO_4 + HC\equiv CNa \longrightarrow EtC\equiv CH + NaEtSO_4$.

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[17] Meinert and Hurd, THIS JOURNAL. 52, 4544 (1930).

[18] Davis, *Ind.* Eng. Chem., *Anal.* Ed., 1, 61 (1929).

Pyrolysis of Ethylacetylene.—The ethylacetylene was pyrolyzed, using the same apparatus that was used for the methylallene experiments. In this case the spiral condenser-receiver was kept at a temperature of $-20°$ so that all of the ethylacetylene which was not changed in the hot zone would be condensed and prevented from passing into the gas collection bottle along with the off-gas from the reaction. The data are given in Table II.

TABLE II

RESULTS OF THE PYROLYSIS OF ETHYLACETYLENE

Run	1	2	3	4
Temperature, °C.	500	550	580	600
Contact time, seconds	34 8	34 5	35.0	30 0
Ethylacetylene used, g.	155	161	18 4	16 4
Ethylacetylene used, cc. of gas	6440	6680	7640	6800
Ethylacetylene recovered, g.	120	8 6	0.0	0 0
Ethylacetylene pyrolyzed, g.	3 5	7.5	18 4	16 4
Ethylacetylene pyrolyzed, cc. of gas	1450	3105	7640	6800
Off-gas not condensed at $-20°$, cc.	750	1750	6600	6800
Entering flow, cc./min.	163	150	146	180
Pressure in tube, mm.	725	732	737	740
Analysis of off-gas, % by volume				
Carbon dioxide	83 0	22 4	7 3	A 0
Acetylenes	..	15 6	12 8	9 4
Gas soluble in 82.5% H_2SO_4	..	7.8	8 7	7 6
Ethylene	..	6 6	9.7	10 8
Hydrogen	..	4 6	13 6	17 0
Paraffins	..	37 4	40 1	43 4
n in C_nH_{2n+2}	..	1 49	1 23	1 18
Percentage decomposition	22 6	47	95–100	95–100
Wt. of liquids formed, g.	1 5	4 0	6.7	6 0
% of liquids formed by wt. of ethylacetylene pyrolyzed	43	53	36 5	36 6
Total volume of gaseous products, cc.				
Acetylenes	..	273	837	640
Gas soluble in 82.5% H_2SO_4	..	137	584	517
Ethylene	..	105	640	735
Hydrogen	..	81	897	1157
Paraffins	..	655	2630	2950
Cc. of gaseous products formed per liter of ethylacetylene pyrolyzed				
Acetylenes	..	884	110	94.2
Gas soluble in 82.5% H_2SO_4	..	43.9	76 5	76.2
Ethylene	..	33 8	83.8	108
Hydrogen	..	26.0	118	170
Paraffins	..	211 0	346	435

The off-gas from Runs 3 and 4 was combined and had a total volume of 11,200 cc. It was passed slowly through a spiral condenser and receiver maintained at a temperature of $-78°$ by a bath of acetone and solid carbon dioxide. About 2 cc. of liquid condensed. This was allowed to vaporize into two fractions by placing the receiver first in an ice-bath and collecting all the gas that came off at this temperature, and then allowing the receiver to warm up to room temperature and collecting this gas. The first fraction consisted of 500 cc. of gas, and the second fraction was also 500 cc. of gas. These two fractions (A and B) gave the following results upon analysis

Fraction	A	B
Acetylenes, %	16.2	41.6
Gas soluble in 82.5% H_2SO_4, %	32.4	47.2
Ethylene, %	12.2	0.0
Carbon dioxide, %	6.5	2.1

From this it can be calculated that the following volumes of substances were present in the two fractions

	A	B
Acetylenes, cc.	81	208
Gas soluble in 82.5% H_2SO_4, cc.	162	236
Ethylene, cc.	61	...

Since the total volume of gas treated in the experiment was 11,200 cc. by adding together the amounts from fractions A and B, it is possible to account for 289 cc. or 2.6% of acetylenes, 398 cc. or 3.5% of hydrocarbons absorbed in 82.5% sulfuric acid and 61 cc. or 0.56% of ethylene. Reference to Table II makes it evident that only about one-fourth of the total acetylenes present in the gas had condensed at −78°. Since methylacetylene boils at −23.8' and ethylacetylene at +8.5°, the uncondensed acetylenes must represent ordinary acetylene (C_2H_2). The fact that a small amount of ethylene, which boils at −103°, was condensed makes it appear probable that some acetylene, which boils at −81°, would also condense. Hence the acetylenes found in fraction A are probably C_2H_2 for the most part.

About one-third of all the hydrocarbons from the pyrolysis which were absorbed in 82.4% sulfuric acid were condensed at −78°. This would certainly include any allene or methylallene which might be present, and would include much propylene as well, which boils at −50°.

In order to ascertain whether there was any methylallene present, all of the acetylenes were removed from a portion of sample B, and the gas which remained was placed in a cylinder inverted in a bath at −5° which completely surrounded it. There was no liquefaction as witnessed by the fact that there was no contraction in volume. Hence the gas of fraction B which was absorbed in 82.5% sulfuric acid could not have been methylallene, nor could any appreciable amounts of dimethylacetylene or butadiene-1,3 have been present. It may have been either allene or propylene. However, taking into account the velocity of the pyrolysis of allene at temperatures above 550°, it is doubtful if any allene would be found in the off-gas from these experiments.

Referring again to Table II, these conclusions indicate that at least 80% of the gases listed as acetylenes consist of acetylene, C_2H_2, the remainder being methylacetylene. The gases absorbed in 82.5% sulfuric acid are considered to be almost entirely propylene, with possibly small amounts of allene, but with no methylallene.

Liquids.—The liquids obtained in the pyrolysis of ethylacetylene were all combined and fractionally distilled. The refractive indices of the various fractions were determined, with these results.

Fraction	Weight, g.	B. p., °C.	n_D^{24}
A	0.5	30–65	....
B	1.0	65–100	1.4720
C	2.0	100–135	1.4925
D	5.0	135–200	1.5242
Residue	8.5		

Fractions B and C were combined and redistilled, and a fraction boiling from 110 to 120° was taken. Its refractive index was 1.4905. The boiling points were not sharp for the different fractions, and the temperature ascended gradually throughout the distillation with no indication of a pure compound distilling over. The very small volume of these fractions made it impossible to purify them further by distillation methods.

The odors and colors of the fractions were very similar to those obtained in the pyrolysis of allene, and especially of methylacetylene. A comparison of the index of refraction data of the corresponding fractions of the liquids obtained from ethylacetylene and methylacetylene shows a marked similarity. They are no doubt compounds of the same type, and there are some indications that some of the same liquids are present from both substances.

Summary

2,3-Dibromo-1-butene and 1,2,2,3-tetrabromobutane have been prepared and their physical properties determined. Methylallene has been prepared in a state of purity and its density and refractive index determined. A new synthesis for ethylacetylene has been developed.

It has been shown that methylallene polymerizes when pyrolyzed, and the presence of a dimer among the polymerization products has been demonstrated. In addition to the polymers, methane, ethane, ethylene, hydrogen, propylene and allene are formed in small amounts.

In the pyrolysis of ethylacetylene it has been shown that from one-third to one-half of the material was converted into liquids which resembled the liquids formed from methylallene, allene and methylacetylene. In addition to the liquids, there were produced paraffinhydrocarbons, hydrogen,

ethylene and propylene in the ratio approximately of 9:3:2:2, as well as small amounts of acetylene, methylacetylene and allene.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE KANSAS AGRICULTURAL EXPERIMENT STATION]

INDICATIONS OF GLUCOSE IN MILK[1]

BY CARRELL H. WHITNAH

RECEIVED NOVEMBER 3, 1930 PUBLISHED JANUARY 12, 1931

The work here reported was started by a request from the Dairy Department to determine if a large increase in the blood sugar of cows would cause the appearance of glucose in the milk. The samples of milk were furnished by the Dairy Department in connection with various projects in which the Department of Chemistry is cooperating.

The milk of lot number one was a composite from all herds supplying milk to the Dairy Department. That of lot number seven was taken separately from three of these herds. The other lots were individual milkings from each of three cows over the intervals indicated.

The official polarimetric method[2] for estimating milk sugar was modified to facilitate the estimation of small amounts of glucose in milk. Fifty cc. of milk was clarified, without further dilution, with 2.5 cc. of official mercuric nitrate solution. The mixture was filtered after standing for five minutes and the rotation of the filtrate measured at 20° in a 20-cm. water-jacketed tube.

Fermentation with yeast, as applied by Raymond and Blanco[3] to other material, was tried as a method of removing any glucose in the milk. To determine whether this method was practicable, 0.5% of glucose was added to a sample of milk, the rotation of which was previously shown not to be changed by treatment with yeast. The extra rotation due to the added glucose was completely removed from 50-cc. samples of this sweetened milk by contact with 3 g. of yeast at 30° in between fifteen and thirty minutes, or with 1 g. of yeast in less than two hours. Samples treated with 3 g. of yeast showed no further change on standing for two hours with the yeast. It was therefore concluded that all the glucose and none of the lactose was removed, and that one hour would be a suitable time for the fermentation.

The yeast was prepared from Fleischmann's baker's yeast by washing and centrifuging five times.[4] The last wash water was found to be clear and free from reducing sugars.

Analyses of 275 samples of milk showed decrease of rotation, after treating 50-cc. portions with 3 g. of yeast for one hour, varying from zero, in 20 cases, to a decrease corresponding to 0.35% of glucose in the milk. In eleven other samples the rotation was observed to increase from 0.01 to 0.07% of the original rotation on treatment with yeast. It is, at present, uncertain whether these apparent increases should be accepted

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[1] Contribution No. 156 from the Department of Chemistry.

[2] Method of Analysis of the Association of Official Agricultural Chemists, 1925.

[3] A. L. Raymond and J. G. Blanco, J. *Biol.* **Chem., 79,** 649 (1928).

[4] M. Somoji, *ibid.,* 75, **33** (1927).

as real and what significance should be given them. The sensitiveness and reliability of the determinations are indicated by the fact that of 566 duplicate determinations 443 checked as closely as the polariscope could be read, *i.* e., less than 0.002% sugar while the average variation in all duplicates was only 0 008%. Thus the method seems sensitive enough to make significant all the measurements reported.

Removal of glucose on treatment with yeast is considered to be the cause of decrease in rotation; first because glucose is generally considered[6] to be the precursor in the blood of the lactose in the milk, and second, because glucose is known to be readily fermented by yeast[6] either in aqueous solutions or in blood.

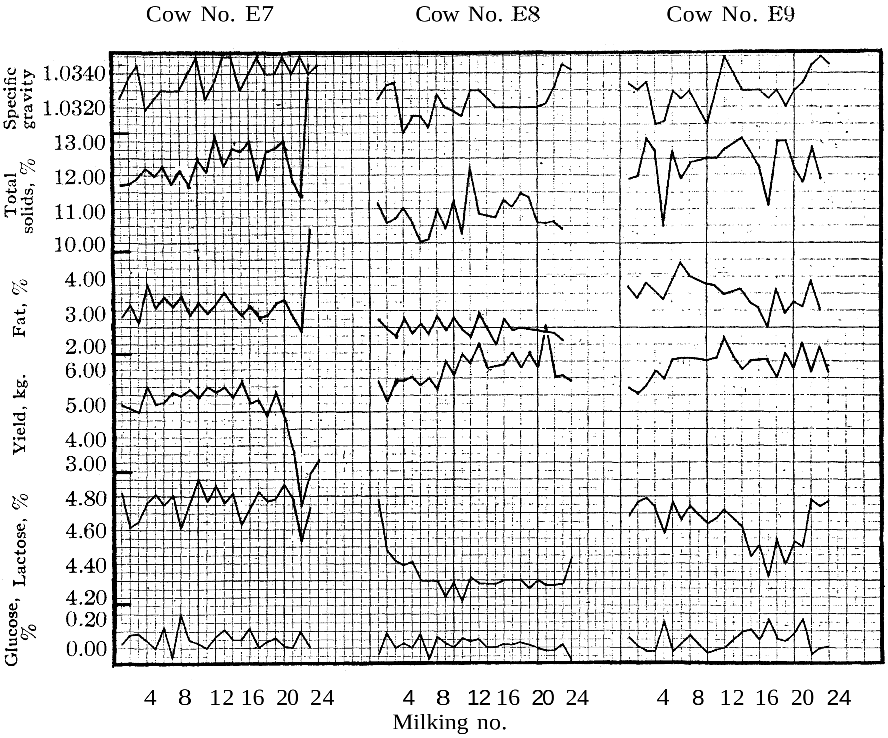

Fig. 1.

Table I shows variations in the glucose content of milk calculated from changes in specific rotation due to fermentation with yeast. The third lot is the only long interval in which all samples apparently contained glucose. This was in the spring shortly after the cows had been turned out to pasture. The observations in the following three lots were on cows receiving dry feed only.

Table II and Fig. 1 indicate simultaneous values in percentage of apparent glucose, percentage of lactose, yield, percentage of fat, percentage of

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[5] E. B. Meigs, *Physiol. Rev.*, 2, 204–211 (1922).

[6] E. Schmidt, F. Trefz and H. Schnegg, *Ber.*, **59B**, *2635* (1926).

TABLE I

APPARENT GLUCOSE IN COW'S MILK

Lot no.	Dates, 1930	Rotation changes as per cent. glucose		Number of milkings where rotation shows		
		Range	Average	Decrease	No change	Increase
1	3/27	0.000	0.000		1 (herd)	
2	3/31–4/4	0.02– .19	.094	32		
		.000	.000		3	
3	4/25–5/13	.07– .35	.195	143		
4	6/5–6/16	.01– .20	.066	45		
		.000	.000		12	
		– .01– .07	– .040			11
5	7/22–7/26	.03– .22	.086	30		
6	8/6	,000	.000		3	
7	8/8	.01– .08	,045	5 (herd)		
		.000	.000		1 (herd)	

total solids, and specific gravity during twenty-four consecutive milkings of three cows. The presence of apparent glucose seems to be independent of any of the other characteristics of the milk which were measured.

TABLE II

APPARENT GLUCOSE CONTENT AND OTHER CHARACTERISTICS OF COW'S MILK

Cow No. E-7

Milking number	Glucose, %	Lactose, %	Yield, kg.	Fat, %	Solids, %	Specific gravity
1	0.02	4.82	4.700	2.80	11.70	1.0325
2	.08	4.61	4.582	3.18	11.76	1.0336
3	.09	4.65	4.481	2.62	11.90	1.0345
4	.05	4.76	5.245	3.80	12.20	1.0318
5	.00	4.81	4.700	3.07	11.97	1.0325
6	.13	4.75	4.770	3.40	12.27	1.0330
7	–.06	4.81	5.075	3.10	11.74	1.0330
8	.20	4.61	4.975	3.44	12.15	1.0330
9	.05	4.76	5.165	2.85	11.66	1.0340
10	.03	4.90	4.907	3.24	12.52	1.0350
11	.00	4.77	5.236	2.90	12.08	1.0325
12	.07	4.87	5.083	3.20	13.19	1.0335
13	.11	4.76	5.243	3.55	12.25	1.0350
14	.05	4.82	4.819	3.14	12.80	1.0350
15	.05	4.63	5.434	2.87	12.45	1.0330
16	.12	4.73	4.750	3.15	13.02	1.0340
17	.00	4.82	4.854	2.79	11.83	1.0350
18	.04	4.77	4.340	2.85	12.70	1.0340
19	.06	4.78	5.110	3.19	12.81	1.0340
20	.01	4.87	4.313	3.30	13.04	1.0350
21	.00	4.78	3.365	2.77	11.86	1.0340
22	.10	4.53	1.689	2.37	11.34	1.0350
23	.00	4.68	2.686	5.40	15.25	1.0340
24			3.120			1.0345

TABLE II *(Continued)*

Cow No. E-8

Milking number	Glucose, %	Lactose. %	Yield, kg.	Fat, %	Solids, %	Specific gravity
1	-0.04	4.78	5.401	2.74	11.18	1.0325
2	.09	4.48	4.813	2.44	10.57	1.0333
3	.00	4.42	5.456	2.25	10.72	1.0335
4	.03	4.39	5.436	2.80	11.04	1.0305
5	.00	4.41	5.534	2.32	10.60	1.0315
6	.09	4.30	5.297	2.62	10.05	1.0315
7	- .07	4.30	5.493	2.29	10.10	1.0308
8	.07	4.30	5.145	2.84	11.01	1.0327
9	.03	4.20	6.000	2.40	10.40	1.0320
10	.00	4.29	5.585	2.82	11.28	1.0318
11	.06	4.17	6.210	2.42	10.28	1.0315
12	.04	4.32	5.944	2.20	12.25	1.0330
13	.05	4.28	6.530	2.95	10.86	1.0330
14			5.800			
15	.00	4.28	5.865	2.00	10.76	1.0320
16	.02	4.30	5.890	2.75	11.28	1.0320
17	.02	4.30	6.256	2.38	11.07	1.0320
18	.03	4.30	5.810	2.48	11.48	1.0320
19	.02	4.25	6.250	2.45	11.37	1.0320
20	.00	4.30	5.826	2.40	10.58	1.0320
21	- .02	4.27	7.086	2.36	10.58	1.0322
22	- .02	4.27	5.563	2.32	10.61	1.0332
23	.02	4.25	5.587	2.11	10.38	1.0345
24	- .08	4.44	5.425			1.0342
			Cow No. E-9			
1	0.06	4.68	5.191	3.70	11.90	1.0334
2	.01	4.77	5.056	3.36	11.96	1.0330
3	- .02	4.79	5.310	3.78	13.12	1.0335
4	- .02	4.74	5.700	4.00	12.68	1.0310
5	.16	4.58	5.478	3.30	10.50	1.0312
6	- .03	4.77	6.050	3.88	12.72	1.0330
7	.02	4.66	6.100	4.44	11.90	1.0325
8	.08	4.74	6.095	4 01	12.37	1.0335
9			6.052			
10	- .03	4.64	6.034	3.78	12.50	1.0315
11	- .01	4.67	6.100	3.74	12.47	
12	.00	4.72	6.700	3.45	12.76	1.0350
13			6.160			
14	.10	4.62	5.783	3.62	13.07	1.0330
15	.11	4.44	6.015	3.20		
16	.05	4.51	6.040	3.09	12.18	1.0330
17	.17	4.32	6.063	2.52	11.12	1.0325
18	.05	4.55	5.554	3.65	13.00	1.0330
19	.04	4.39	6.252	2.90	13.00	1.0320
20	.09	4.53	5.800	3.25	12.20	1.0330

TABLE II *(Concluded)*

Milking number	Glucose, %	Lactose, %	Yield, kg.	Fat, %	Solids, %	Specific gravity
21	.17	4.50	6.565	3.11	11.76	1.0335
22	− .04	4.78	5.641	3.87	12.82	1.0345
23	.00	4.74	6.444	3.01	11.86	1.0350
24	.01	4.77	5.680			1.0340

Summary

A method for estimating small amounts of glucose in milk has been developed, which depends on selective fermentation of the glucose and measurement of the rotary power of fermented and unfermented milk.

Changes in rotary power corresponding to glucose percentages varying from zero to 0.35% of glucose have been found in normal cow's milk.

MANHATTAN, KANSAS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE IDENTIFICATION OF PHENOLS

BY C. FREDERICK KOELSCH

RECEIVED NOVEMBER 3, 1930 PUBLISHED JANUARY 12, 1931

Reagents which have been recommended for the identification of phenols are diphenylcarbamine chloride,[1] *p*-nitrobenzyl bromide[2] and 3,5-dinitrobenzoyl chloride.[3] Since none of these reagents in the hands of the inexperienced student has given entirely satisfactory results, the characterization of phenols by the use of chloro-acetic acid has been developed in this Laboratory.

Chloro-acetic acid reacts smoothly with phenols in aqueous sodium hydroxide giving good yields of the sodium salts of aryloxyacetic acids. The acids themselves are crystalline solids easily purified by recrystallization from water. One gram of a phenol furnishes an amount of the derivative sufficient for the determination of its neutral equivalent, often a valuable aid in identification, in addition to its melting point.

The experimental procedure is quite simple. To a mixture of 1.0 g. of the phenol with 3.5 ml. of 33% sodium hydroxide is added 2.5 ml. of a 50% chloro-acetic acid solution; if necessary, a little water is added to dissolve the sodium salt of the phenol. The test-tube containing the solution is stoppered loosely and heated for one hour in a gently boiling water-bath. The solution is cooled, diluted, acidified to congo red with a mineral acid, and extracted once with ether. The ether extract is washed once with a little water, and the aryloxyacetic acid is removed by washing with dilute

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[1] Herzog, Ber., 40, 1831 (1907).

[2] Reid, THIS JOURNAL, 39, 304 (1917); Lyman and Reid, *ibid.*, 42, 615 (1920).

[3] Brown and Kremers, *J. Am. Pharm. Assocn.*, 11, 607 (1922).

sodium carbonate solution. Acidification of this extract gives the free acid, which is recrystallized from water.

The accompanying table contains the data which have been observed on the aryloxyacetic acids prepared in this Laboratory. Those acids for which no reference is given are new compounds. As was expected,[4] no nitrophenoxyacetic acids were isolated when o- or *p*-nitrophenols were used, and the yield was unsatisfactory when m-nitrophenol was used.

TABLE I

THE MELTING POINTS AND NEUTRAL EQUIVALENTS OF A FEW ARYLOXYACETIC ACIDS

	Phenol	Yield, g	Neut equiv		M p, °C (uncorr)	
			Obs.	Calcd.	Obs	Literature
1	Phenol	0 3 8	155	152	98–99	98 99[b]
2	o-Cresol	65	166	166	151–152	151–152"
3	m-Cresol	1 01	168	166	102–103	102"
4	*p*-Cresol	0 75	167	166	134–136	135–136[e]
6	*o*-Chlorophenol	37	185 5	186.5	143–145	.....
6	na-Chiorophenol	40	185	186 5	108–110	.....
7	*p* Chlorophenol	60	187	186 5	15.5156 5	151–152[f]
8	*o*-Bromophenol	26	230	231	131-143	142 5–143[g]
9	m-Brornophenol	.47	234	231	107–108 5	.. ..
10	*p*-Bromophenol	.60	228	231	157	153–154[h]
11	o-Iodophenol	.20	277	278	134–135	.. .
12	m-Iodophenol	.36	279	278	114–115 5	....
13	p-Iodophenol	.48	278	278	154–156	155–156[i]
14	o-Methoxyphenol	.41	180	182	116–116 5"	121'
15	m-Methoxyphenol	.63	182	182	111–113"	115–118[k]
16	*p*-Methoxyphenol	.56	182	182	110–112	
17	Thyrnol	.45	208	208	148–149	147–148[l]
18	Carvacrol	.45	211	208	150–151	149""
19	a-Naphthol	.50	199	202	191–192	190[n]
20	β-Naphthol	.50	203	202	153–154 5	156[o]

[a] Despite alternate recrystallizations from water and from benzene, the melting point remained unchanged, [b] Hantzsch, *Ber* , **19,** 1296 (1886); [c] Oglialoro and Cannone, *Gazz. chim ital* , **18,** 511 (1888); [d] Oglialoro and Forte, *ibid.*, **20,** 508 (1890); [e] Gabriel, *Ber* , **14,923** (1881); [f] Peratoner, *Gazz* chim. *ital.*, **28,** I, 239 (1898); [g] Auwers and Haymann, *Ber* , 27, 2799 (1894); [h] Pritzsche, J. *pmkt. Chem.*, [2] **20,** 295 (1879); [i] Marveli, Gambetta and Rimini, *Gazz* chzm. *ital.*, **50,** 1, 173 (1920); [j] Auwers and Haymann, *Ber* , **27,** 2804 (1894); [k] Gilbody, Perkin and Yates, J. *Chem. Soc* , 79, 1409 (1901); [l] Spica, *Gazz* chzm *ital* , **10,** 341 (1880); [m] Spica, *ibid.*, p. 345; [n] Spica, *ibid.*, 16, 438 (1886); [o] Spitzer, *Ber* , **34,** 3191 (1901).

The assistance of Professor S. M. McElvain is gratefully acknowledged.

Summary

Aryloxyacetic acids, easily prepared from chloro-acetic acid and phenols are recommended as derivatives for the identification of the latter compounds.

MADISON, WISCONSIN

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[4] *Cf.* Hewitt, Johnson and Pope, J. *Chem. Soc.*, **103,** 1630 (1913).

[CONTRIBUTION FROM THE DEPARTMENTS OF AGRICULTURAL CHEMISTRY AND AGRICULTURAL BACTERIOLOGY, UNIVERSITY OF WISCONSIN]

GLUCURONIC ACID, A CONSTITUENT OF THE GUM OF ROOT NODULE BACTERIA[1]

BY E. W. HOPKINS, W. H. PETERSON AND E. B. FRED

RECEIVED NOVEMBER 6, 1930 PUBLISHED JANUARY 12, 1931

In a previous paper[2] data were presented which demonstrated that glucose is a product of hydrolysis of the gums produced by the bacteria of red clover, alfalfa and pea, and that uronic acid is also a constituent of these gums and comprises from 4.1 to **25.3%** of the weight of the gum. Besides the analytical data, qualitative tests indicated the presence of a uronic acid. When the gum hydrolysate was neutralized with barium hydroxide and poured into ethyl alcohol, a precipitate formed which possessed reducing properties, left a considerable ash on ignition, and gave a strong uronic acid test with naphthoresorcinol. The uronic acid did not yield mucic acid when oxidized with nitric acid and hence was not galacturonic acid.

The nature of the unknown uronic acid has been investigated more thoroughly and, on the basis of the evidence which will be presented in this paper, it is concluded that the unknown acid is glucuronic.

Experimental

Identification of the Uronic Acid.—The gum was produced by pure cultures of pea and red clover bacteria, and was prepared as described in a previous paper.[2] The dried gum was taken into solution with 5% (by weight) sulfuric acid, and was hydrolyzed by heating for two hours in an autoclave at fifteen pounds steam pressure. After neutralizing the hot solution with barium carbonate, the barium sulfate was filtered off and well washed. The filtrate was concentrated to about one-tenth of the original volume and poured into four volumes of 95% alcohol. The precipitate which formed was filtered off. The filtrate was concentrated to a small volume and a second precipitate was obtained by pouring into alcohol. The combined precipitates of crude uronic acid were taken into solution in a small volume of water and an excess of sulfuric acid was added. Upon pouring this solution into four volumes of 95% alcohol, a precipitate of inorganic impurities formed. The alcohol was removed by evaporation and the sulfuric acid precipitated with barium hydroxide. The filtrate from the barium sulfate was neutralized at the boiling point with barium hydroxide in order to insure the complete neutralization of any uronic acid lactone. The solution was then decolorized, concentrated and the barium salt of the uronic acid precipitated with alcohol. The product still retained a slightly yellow color, but it was sufficiently pure for the preparation of the osazone derivative.

The *p*-bromophenylhydrazone of glucuronic acid has been used by Neuberg[3] as a means of identification, but Goldschmiedt and Zerner[4] reported difficulty in the purification of this derivative, and found that the alkaline earth salts of glucuronic acid furnished a better starting material for the preparation of a suitable derivative. They

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[1] Herman Frasch Foundation Research in Agricultural Chemistry, Paper No. 15.

[2] E. W. Hopkins, W. H. Peterson and E. B. Fred, THIS JOURNAL, 52,3659 (1930).

[3] C. Neuberg, *Ber. deut. Chem. Ges.*, **33,** 3315 (1900).

[4] G. Goldschmiedt and E. Zerner, *Monatsh*, **33,** 1217 (1912).

prepared the *p*-bromophenylosazone and found this compound could he readily purified and that it gave nitrogen and base analyses which checked well with the calculated values. The use of this derivative as a means of identification possessed particular advantages in our work since the separation and purification of free uronic acid from its salt can be accomplished only with considerable loss of material. Therefore the *p*-bromophenylosazone of the barium salt of the uronic acid was prepared and the melting point and the barium and nitrogen contents of this derivative were determined.

Uronic Acid of Preparation 6 (Gum from Red Clover Nodule Bacteria).—The gum was hydrolyzed and the barium salt of the uronic acid purified by the methods already described. This purified barium salt was used in the preparation of the p-bromophenylhydrazine derivative, as follows: barium salt of the uronic acid 1 part, p-bromophenylhydrazine hydrochloride 3 parts, barium acetate 4 parts and water 70 parts. The mixture was heated for two minutes in a boiling water-bath, shaken well, and rapidly filtered. The turbid yellow filtrate was treated with 3 cc. of glacial acetic acid, and again heated in a boiling water-bath. After ten to twenty minutes' heating yellow crystals began to separate. Further crops of crystals were obtained by continued heating, but the melting point of these later crops varied but little from that of the first. The crystals were filtered off, washed well with water, and with boiling absolute ethyl alcohol. The melting point of the derivative was 216". Goldschmiedt and Zerner give the melting point of the p-bromophenylosazone of barium glucuronate as 215–217°. The same derivative of glucuronic acid was prepared and its melting point found to be 216°.[5] The melting point of a mixture of the known derivative with the unknown was the same as that of the derivatives separately, 216".

The osazone was analyzed for nitrogen and barium by the micro methods of Pregl.[6]

Anal. Subs., 6.090 mg.: N_2, 0.504 cc. (24°, 746 mm.). Subs., 7.335 mg.: $BaSO_4$, 1.430 mg. Calcd. for $(C_{18}H_{17}O_5N_4Br_2)_2Ba$: N, 9.37; Ba, 11.49. Found: N, 9.35; Ba, 11.47.

Uronic Acid Preparation 8 (Gum from Pea Nodule Bacteria).—The gum was hydrolyzed, the barium salt of the uronic acid was purified, and the p-bromophenylosazone prepared in the manner already described. The melting point of the preparation was 216" and no depression in the melting point of the same derivative of glucuronic acid occurred when the two were mixed together. Analyses for nitrogen and barium gave the following results.

Anal. Subs., 7.300 mg.: N_2, 0.615 cc. (24°, 746 mm.). Subs., 4.960 mg.: $BaSO_4$, 0.980 mg. Calcd. for $(C_{18}H_{17}O_5N_4Br_2)_2Ba$: N, 9.37; Ba, 11.49. Found: N, 9.52; Ba, 11.62.

The melting point and the barium and the nitrogen content of the p-bromophenylosazone agree with those of the same derivative of glucuronic acid.

Further Evidence of the Identity of the Sugar Produced by Hydrolysis of the Gum.—In a previous paper[Z] it was reported that the sugar constituent of the gums was glucose, as was indicated by fermentation tests and the melting point of the phenylosazones. In the preparation of the glucuronic acid considered in this paper, the sugar obtained on hydrolysis was a matter of minor concern, but since material was available, it seemed worth while again to determine the identity of the sugar.

Sugar of Preparation 8 (Gum from Pea Nodule Bacteria).—After concentra-

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[5] The authors desire to express their gratitude to Dr. Armand J. Quick of the Cornell University Medical College for placing at their disposal the glucuronic acid used in this test.

[6] The authors are indebted to Professor Karl Paul Link of the Agricultural Chemistry Department for the micro analyses given in this paper.

tion of the sugar solution to a small volume, glacial acetic acid was added. Crystallization of the sugar took place rapidly and the sugar was purified by recrystallization from acetic acid. The pure product was dried thoroughly in a vacuum oven and a polarization of the sugar made: 0.5005 g. was dissolved in water and after adding a drop of strong ammonia the volume was made up to 25 cc. The rotation in a 200-mm. tube at 24.5" was found to be +6.1° Ventzke; specific rotation: found, +52.7°, required for d-glucose, +52.7°.[7]

The phenylosazone was prepared and was found to have a melting point of 204". The nitrogen content of the phenylosazone was as follows.

Anal. Subs., 4.515 mg.: N_2, 0.6566 cc. (24°, 741.7 mm.). Calcd. for $C_{18}H_{22}N_4O_4$: N, 15.65. Found: N, 16.25.

Although the nitrogen content of the phenylosazone does not agree as well with the calculated value as is desirable in a good derivative, the other evidence presented, i. e., the specific rotation of the crystallized sugar, and the results of the fermentation tests reported in the previous paper[2] give clear evidence that the sugar is glucose.

Sugar of Preparation 6 (Gum from Red Clover Nodule Bacteria).—An attempt was made to crystallize the sugar obtained by hydrolysis of this preparation, but without success. One of the solutions was clarified with basic lead acetate and another was dehydrated in vacuo and the friable residue taken up in absolute methyl alcohol, but both treatments failed to remove some substance which interfered with crystallization. The phenylosazone, however, was prepared without difficulty. The melting point of the osazone was 204°. Analysis gave the following figures for nitrogen.

Anal. Subs., 4.100 mg.: N_2, 0.5831 cc. (24°, 741.7 mm.). Calcd. for $C_{18}H_{22}N_4O_4$: N, 15.65. Found: N, 15.89.

The nitrogen content of this osazone is within the limits of error usual in such preparations. This evidence together with the results of the fermentation tests previously reported[2] indicates that here, as in the pea gum, glucose is a constituent of the gum.

Discussion

Although glucose and glucuronic acid were the products of hydrolysis of both pea and red clover gums, it does not appear that these two gums are identical chemical entities. Certain differences between them were observed. Less reducing sugar as glucose was obtained from pea gum than from the red clover gum. After fermentation of the sugars by yeast and bacteria, the hydrolysate of pea gum contained a larger amount of unfermentable reducing substance. A further point of difference was evidenced by the unsuccessful attempts to crystallize the sugar of red clover gum in contrast to the comparative ease with which crystallization of the pea gum sugar took place. Thus, when considered from the point of view of their hydrolytic products, there are differences in the gums in spite of their apparent similarity. These products of hydrolysis are the same as those obtained by Heidelberger and associates[8] from the soluble specific substance of Type III Pneumococcus. However, these workers found in the

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[7] C. A. Browne, "A Handbook of Sugar Analysis," New York, 1912, p. 173.

[8] (a) M. Heidelberger, W. F. Goebel and O. F. Avery, J. *Exptl. Med.*, 42, 727 (1925); (b) M. Heidelberger and W. F. Goebel, J. *Biol. Chem.*, 74, 613 (1927); (c) M. Heidelberger, *Physiol. Rev.*, 7, 107 (1927).

hydrolytic products an aldobionic acid precipitable by basic lead acetate. Since in our work the sugar solution was purified by repeated precipitation with 95% ethyl alcohol, such an acid might have been overlooked. Ehrlich and von Sommerfeld[9] report a di-uronic acid obtained by the hydrolysis of pectinic acid. This acid appeared as an insoluble mass in the hydrolysate. In our work a very small amount of insoluble matter was observed in the acid solution after hydrolysis and this material apparently did possess acidic properties. However, the method of hydrolysis used was more drastic than that employed by either Heidelberger and Goebel or Ehrlich and von Sommerfeld, as it was desired to obtain only the products of complete hydrolysis. If compounds of either of these types were present, they must have constituted only a small part of the products of hydrolysis.

Summary

Glucuronic acid has been identified as a constituent of the gum produced by the root nodule bacteria of pea and red clover. The gum was subjected to acid hydrolysis and the glucuronic acid separated from the hydrolysis products as the barium salt. The *p*-bromophenylosazone of this salt had the melting point and the barium and the nitrogen content required for this derivative of glucuronic acid.

The sugar produced by hydrolysis of the gum of the pea bacteria was crystallized, and its specific rotation agreed with that of glucose. In the case of the sugar from the gum of the red clover bacteria, crystallization could not be effected. However, the phenylosazone of this sugar possessed the melting point and the nitrogen content required for phenylglucosazone.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE SCHOOL OF PHARMACY AND THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

THE MIGRATION OF ACYL FROM SULFUR TO NITROGEN

BY H. P. LANKELMA AND ALBERT E. KNAUF

RECEIVED NOVEMBER 6, 1930 PUBLISHED JANUARY 12, 1931

The work of Raiford,[1] from a study of sixteen different substituted *o*-aminophenols, has shown that when the radicals acetyl and benzoyl are introduced, identical diacyl derivatives are obtained regardless of the order of introduction. This clearly involves a migration of acyl between oxygen and nitrogen during acylation. The present investigation was undertaken to determine whether a similar migration of the radicals acetyl and benzoyl would take place between sulfur and nitrogen in an o-aminothiophenol.

The base employed, 2-amino-4-chloro-thiophenol is readily prepared and isolated in the form of the hydrochloride, by reducing 4,4′-dichloro-2,2′-

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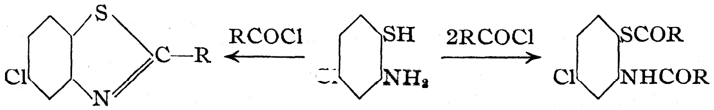
[9] F. Ehrlich and R. von Sommerfeld, *Biochem.* Z., 168, 263 (1926).

[1] See papers of Raiford, THIS JOURNAL (1919–1926).

dinitrodiphenyldisulfide with tin and hydrochloric acid. The acylation of the hydrochloride in dimethylaniline, with acetic anhydride or benzoyl chloride easily could be controlled to give either the diacyl derivative or benzothiazole. Heating the mixture at the temperature of tha water-bath gave a smooth conversion to the diacyl derivative; upon boiling the mixture, however, only benzothiazole was obtained.[2]



2-Benzoylamino-4-chlorothiophenol and 2-acetylamino-4-chloro-thiophenol, upon drying for several hours in a desiccator or upon recrystallization from alcohol, were completely converted into the corresponding benzothiazoles.[3] Hofmann[4] prepared 2-phenylbenzothiazole by heating *o*-aminothiophenol hydrochloride with benzoyl chloride. He called attention to the probable formation of the N-benzoyl derivative as an intermediate product but did not isolate it. Reissert[5] upon saponifying 2-benzoylaminophenyl thiobenzoate obtained a product which upon recrystallization from alcohol proved to be 2-phenyl-benzothiazole. He reports no melting point for the crude product. It is probable that the initial product was the N-benzoyl derivative, which upon recrystallization formed the benzothiazole.

2-Benzoylamino-4-chlorothiophenol gave upon treatment with acetyl chloride a different diacyl derivative from that obtained by treating 2-acetylamino-4-chlorothiophenol with benzoyl chloride. This shows that no migration of acyl occurs during acylation.

Saponification of the two isomeric benzoyl acetyl derivatives gave the same product, 2-benzoylamino-4-chlorothiophenol, which was identified in one case as the corresponding benzothiazole. This shows that the benzoyl radical displaces acetyl from nitrogen upon saponification of 2-acetylamino-4-chlorophenyl thiobenzoate.

Experimental

2-Amino-4-chlorothiophenol Hydrochloride.—4,4′-Dichloro-2,2′-dinitrodiphenyldisulfide prepared by the method of Blanksma[6] was suspended in five times its weight of alcohol and reduced with tin and hydrochloric acid. The best yields were obtained by stirring the mixture at a temperature of about 70°. Above this temperature a por-

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[2] A further study of the acylation of this base has been made and will be reported in a later communication.

[3] Mills and Whitworth, *J. Chem. Soc.*, 2738 (1927), have found that 2-cinnamoylaminothiophenol may be recrystallized from alcohol unchanged.

[4] Hofmann, *Ber.*, 12, 2365 (1879).

[5] Reissert, *ibid.*, **38**, 3431 (1905).

[6] Blanksma, *Rec. trav. chim.*, 20, 131 (1901).

tion of the aminothiophenol was further reduced, with the liberation of hydrogen sulfide. The resulting solution was filtered, the filtrate evaporated to about one-third its volume, and the hot solution treated with an equal volume of concentrated hydrochloric acid. Upon cooling, the hydrochloride separated out, contaminated with tin salts. It was purified by reprecipitation from alcohol with hydrochloric acid. It separated in firm colorless or straw colored needles; yield, 55–60%.[7] That this product is 2-amino-4-chlorothiophenol hydrochloride was shown by the fact that it is soluble in cold aqueous alkali, and by the analysis for sulfur.

Anal. Calcd. for $C_6H_8NCl_2S$: S, 16.34. Found: S, 16.27.

The hydrochloride was converted into the free base by the action of an excess of ammonium carbonate solution. The free base separated as a light yellow precipitate, m. p. 198–201° with decomposition.8 Upon oxidation with ferric chloride it is converted into 4,4′-dichlorodi-*o*-thioaniline, m. p. 118–119°.[9] The free base is very rapidly oxidized by the air to the alkali-insoluble disulfide.

2-Phenyl-5-chlorobenzothiazole.—One gram of 2-amino-4-chlorothiophenol hydrochloride was dissolved in 8 cc. of dimethylaniline and 1.2 g. of benzoyl chloride added. The mixture was boiled for thirty minutes. The thiazole was precipitated with dilute hydrochloric acid. It separated as colorless plates, insoluble in dilute alkali; yield, 1.2 g. Upon recrystallization from alcohol it separated in small colorless plates of m. p. 139°.

Anal. Calcd. for $C_{13}H_8NClS$: S, 13.05. Found: S, 13.26.

2-Methyl-5-chlorobenzothiazole.—This product resulted when the hydrochloride was treated with acetic anhydride by the method described above. The benzothiazole was extracted from the acidified solution with ether. One gram of hydrochloride gave 0.5 g. of benzothiazole, m. p. 65–67°. Upon recrystallization from alcohol it separated in thin colorless plates melting at 68–69°.

Anal. Calcd. for C_8H_6NClS: S, 17.45. Found: S, 17.36.

2-Benzoylamino-4-chlorophenyl **Thiobenzoate.**—A mixture of 1 g. of 4-chloro-2-aminothiophenol hydrochloride, 1.8 g. of benzoyl chloride and 5 cc. of dimethylaniline was heated on a water-bath for ten minutes. The dibenzoyl derivative was precipitated by hydrochloric acid; 1.35 g. of product melting at 140–154° was obtained. It was recrystallized from a mixture of benzene and alcohol from which it separated in colorless plates of m. p. 158–159°.

Anal. Calcd. for $C_{20}H_{14}SNClO_2$: S, 8.72. Found: S, 9.07.

2-Benzoylamino-4-chlorothiophenol.—0.74 g. of 2-benzoylamino-4-chlorophenyl thiobenzoate was saponified by allowing it to stand at room temperature with an excess of potassium hydroxide in alcohol. Upon diluting with water and acidifying, the monobenzoyl derivative separated as a crystalline white solid, which upon drying melted at 105–106°; yield, 0.45 g. This compound was soluble in dilute aqueous sodium hydroxide and was precipitated unchanged on acidifying.

Anal. Calcd. for $C_{13}H_{10}ONClS$: S, 12.11. Found: S, 12.29.

Upon recrystallization from alcohol or ether this substance was completely converted into the alkali insoluble 2-phenyl-5-chlorobenzothiazole, m. p. 139".

2-Acetylamino-4-chlorophenyl **Thioacetate.**—One and four-tenths grams of 2-amino-4-chlorothiophenol hydrochloride and 2.0 cc. of acetic anhydride were treated

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[7] The hydrochloride has a pronounced vesicant action upon the skin.

[8] Hodgson and Wilson, J. Chem. *Soc.*, **127**, 443 (1925), report 120° as the melting point.

[9] Hodgson and Wilson, Ref. 8, report a melting point of 116° for this substance.

as described under benzoylation of the base: 1.4 g. of product melting at 149–150° was obtained. It was recrystallized from alcohol, from which it separated as soft white needles melting at 150–151°.

Anal. Calcd. for $C_{10}H_{10}O_2NCl$: S, 13.17. Found: S, 12.90.

2-Acetylamino-4-chlorothiophenol.—One gram of 2-acetylamino-4-chlorophenyl thioacetate upon saponification with potassium hydroxide in alcohol gave 0.6 g. of monoacetyl derivative, m. p. 92–94°. This product was soluble in dilute sodium hydroxide solution and was precipitated unchanged on acidifying.

Anal. Calcd. for C_8H_8ONClS: S, 15.90. Found: S, 15.74.

This substance upon recrystallizing from alcohol separated in colorless plates, m. p. 68–69°. When melted with a sample of 2-methyl-4-chlorobenzothiazole the mixture melted without depression.

2-Acetylamino-4-chlorophenyl **Thiobenzoate.**—0.72 g. of 2-acetylamino-4-chlorothiophenol upon benzoylation in dimethylaniline with 0.70 g. of benzoyl chloride gave 1.05 g. of product melting at 137–142". Upon recrystallization from alcohol it separated in soft colorless needles of m. p. 141–142°.

Anal. Calcd. for $C_{15}H_{12}O_2NClS$: S, 10.49. Found: S, 10.55.

2-Benzoylamino-4-chlorophenyl Thioacetate.—0.58 g. of 2-benzoylamino-4-chlorothiophenol and 1.0 g. of acetyl chloride were dissolved in a few drops of dimethylaniline and the mixture heated for ten minutes on a water-bath. Upon acidifying, the diacyl derivative was precipitated: 0.55 g. of product melting at 108–116° was obtained. Upon recrystallization from alcohol it separated as long colorless needles melting at 129–130°. A mixture of this material with the isomeric 2-acetylamino-4-chlorophenyl thiobenzoate melted at 108–116°, showing that they are different substances.

Anal. Calcd. for $C_{15}H_{12}O_2NClS$: S, 10.49. Found: S, 10.84.

Saponification of **2-Acetylamino-4-chlorophenyl Thiobenzoate.**—Eight-tenths gram of this substance was saponified with excess potassium hydroxide in alcohol. The monoacyl derivative obtained melted at 60–90° and was soluble in cold aqueous sodium hydroxide. Upon recrystallization from alcohol it melted at 138–139°. When melted with a sample of 2-phenyl-5-chlorobenzothiazole, m. p. 139°, the mixture melted at 138–139°, showing the identity of the two substances.

Saponification of 2-Benzoylamino-4-chlorophenyl **Thiobenzoate.**—0.46 g. of this substance upon saponifying with excess potassium hydroxide in alcohol gave 0.16 g. of product melting at 89–93°. Upon purifying by reprecipitating from aqueous sodium hydroxide it melted at 100–102°. A mixture of this product with 2-benzoylamino-4-chlorothiophenol melted without depression.

Summary

1. N-Acyl derivatives of 2-amino-4-chloro-thiophenol have been prepared. These lose water very readily to form the corresponding benzothiazoles.

2. No rearrangement of acetyl and benzoyl between sulfur and nitrogen occurs upon acylation of the N-acyl derivative of the o-aminothiophenol. This is unlike the typical behavior of an o-aminophenol.

3. Upon saponification of 2-acetylamino-4-chlorophenyl thiobenzoate a migration of benzoyl from sulfur to nitrogen occurs.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

DEGUELIN. I. THE PREPARATION, PURIFICATION AND PROPERTIES OF DEGUELIN, A CONSTITUENT OF CERTAIN TROPICAL FISH-POISONING PLANTS

BY E. P. CLARK

RECEIVED NOVEMBER 7, 1930 PUBLISHED JANUARY 12, 1931

In two recently published reports concerning the constituents of some tropical fish-poisoning plants[1,2] attention was directed to a pale green substance which crystallizes in rod-like plates and melts at 171°. This material, which is highly toxic to fish, is an active constituent of derris and cubé roots, the leaves of *Cracca (Tephrosia) vogelii* and the roots of *Cracca (Tephrosia) toxicaria*.

For purposes of convenience the compound has been termed deguelin, derived from *Deguelia*, the generic name, which, under the American code of botanical nomenclature, supersedes that of derris.

Although deguelin occurs abundantly in cubé and derris roots, its preparation in a chemically pure condition is accomplished with difficulty, which fact has seriously limited the supply of material for study. However, with the information now available it is possible to state that deguelin is a dimethoxylactone, $C_{23}H_{22}O_6$. Some derivatives of the substance have been prepared and, in a preliminary way, its effectiveness as an insecticide has been investigated[3] This communication describes the procedure used in the preparation and purification of the compound, records some of its chemical and physical properties and presents the data upon which the statements regarding its composition and nature have been based.

Deguelin occurs in the non-crystallizable extractives of the four previously mentioned plant materials. Apparently, however, it exists in some form of combination, since it and the constituents with which it is associated are obtained only when the non-crystalline material, dissolved preferably in methyl or ethyl alcohol, is treated with an alkali. In many of the common solvents, the solubilities of all the constituents, including deguelin, are essentially the same, rendering the purification of any one of the substances difficult.

Deguelin showed no optical activity, but it may have existed in the plant in an optically active state and the drastic alkali treatment might have caused racemization. This point has not yet been studied.

When deguelin was first prepared it was purified by repeated recrystallization until it had a constant melting point of 165°. This material was optically uniform, and analytical data showed the composition indicated

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[1] Clark, *Science*, 71, 396 (1930).

[2] Clark, THIS JOURNAL, 52, 2461 (1930).

[3] Davidson, *J. Econ. Entomol.*, 23, 877 (1930).

by its formula to be constant. Later, in purifying another lot, the melting point constantly dropped until 165° was reached. Upon further recrystallization the melting point rose until at 171° it was constant. Both preparations, that is, the compound melting at 171° and that melting at 165°, had identical optical properties and gave identical analytical data. After obtaining the substance melting at 171° it has been impossible, so far, to obtain a pure sample melting at 165°. The melting point of 171° has, therefore, been recorded for the material.

A reaction of deguelin useful in permitting an attack upon the molecule is its oxidation with potassium ferricyanide. Under properly controlled conditions the reaction proceeds smoothly, yielding a yellow compound, dehydrodeguelin, $C_{23}H_{20}O_6$. On further oxidation with chromic acid, this substance forms dehydrodeguelone, $C_{23}H_{18}O_7$. This is interpreted as indicating an oxidation of a methylene to a carbonyl group.

Dehydrodeguelin reacts with alcoholic potassium hydroxide, forming a phenolic monocarboxylic acid, $C_{23}H_{24}O_8$. The reaction shows the presence in the molecule of a lactone group, but since it involves the addition of two moles of water instead of one, as would be expected, the reaction is abnormal and is analogous to the results obtained by Butenandt with dehydrorotenone.[4]

Evidence of a phenolic hydroxyl group in this acid, which has been designated as deguelic acid, was given by the claret color developed when an alcoholic solution of the acid was treated with ferric chloride. Attempts to form a crystalline acetyl derivative of the acid by using acetic anhydride and sodium acetate were unsuccessful. Instead, ring closure and dehydration occurred, resulting in the regeneration of the mother substance, dehydrodeguelin.

Further work upon this insecticide is in progress.

Experimental

The rotenone in a concentrated ethereal extract of derris root was removed by crystallization, and the mother liquors were concentrated to a thick sirup, practically free from ether; 100 g. of this material was dissolved in 300 cc. of hot methanol and treated with 20 cc. of aqueous 10% solution of sodium hydroxide. In a short time crystallization began and after twenty-four hours 27.5 g. of crude product was removed. This material was a mixture of several substances, three of which predominated, namely, toxicarol, deguelin and tephrosin.

A rough separation of toxicarol was obtained as follows. The crude mixture was dissolved in the minimum quantity of boiling chloroform. The solution was filtered through norit, and again heated to its boiling point. Twelve volumes of boiling alcohol were then added. The solution was vigorously boiled until it was practically free from chloroform, and by that time most of the toxicarol had separated. The crystals filtered from the boiling solution consisted of 10 g. of impure toxicarol. As the mother liquors cooled, 5 g. of light yellow crystals separated, whose melting point was around 168°. This fraction, which is richest in deguelin, was subjected to fractional crystalliza-

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[4] Butenandt, *Ann.*, 464, 372 (1928).

tion from boiling 95% alcohol. As purification proceeded the melting point generally dropped somewhat and then rose eventually to 171°.

The substance crystallizes in plate-like rods many of which are six-sided. Its indices of refraction are: η_α, 1.570; η_β, 1.590 (common) and η_γ, $>$ 1.739 both ±0.003. The extinction is inclined, and the elongation is negative. Most of the crystals do not extinguish sharply when examined in parallel polarized light with crossed nicols.[5]

Anal. Calcd. for $C_{23}H_{22}O_6$: C, 70.03; H, 5.63; OCH_3 (2), 15.7. Found: C, 69.99; H, 5.63; OCH_3, 15.8.

There is much deguelin in the impure toxicarol and in the mother liquors from the crystalline material used for fractionation. However, the difficulty involved in separating it as such is too great for it to be of practical value. Some of the deguelin fractions obtained after roughly removing toxicarol may have melting points higher or even lower than 168, depending largely upon the quality of the derris root employed.

Deguelin from Cubé Root.—The non-crystallizable extractives from cubé root when treated with sodium hydroxide in the manner just outlined yield principally a mixture of deguelin and tephrosin. There is also a small quantity of a yellow substance present, but deguelin is much more readily obtained pure from cubé than from the crystalline mixture derived from derris root. Also, sodium carbonate may be substituted for sodium hydroxide to induce the crystallization of the mixture of compounds under discussion. With sodium carbonate crystallization is generally slower, and the two main constituents separate in large crystals, enabling one to make a rough mechanical separation, and thereby simplifying the purification of deguelin. The following experiment is representative of what may be obtained with a good specimen of cubé roots.

Rotenone mother liquors from 5.2 kg. of cubé roots were concentrated to a thick sirup. This material, which weighed 560 g., was dissolved in 11 liters of hot methanol, and 55 g. of dry sodium carbonate was added. The mixture was stirred occasionally for an hour and then allowed to crystallize for two days. The product was removed by filtration and washed first with methanol, and then with water to remove the excess of sodium carbonate. Upon suspending the mixture in methanol, tephrosin, which consisted of heavy prisms, quickly settled to the bottom of the container, and deguelin, in the form of thin plate-like rods, remained suspended sufficiently long to be decanted. The yield was 92 g. of crude tephrosin and 83 g. of deguelin. Upon concentrating the mother liquors under reduced pressure, 98 g. of a mixture of deguelin and tephrosin was obtained. Since this material was more valuable as a source of tephrosin, it was used for this purpose. The purity of the deguelin fraction was such that one recrystallization from *n*-butanol followed by two recrystallizations from ethanol gave a product whose melting point was 171° and which possessed the same optical properties recorded for deguelin from derris.

Dehydrodeguelin.—Ten grams of deguelin dissolved in 500 cc. of boiling ethanol was treated with 150 cc. of a hot aqueous solution of 18 g. of potassium ferricyanide and 2.8 g. of potassium hydroxide. The mixture was allowed to stand until the next day and then quickly diluted with 1.5 liters of water. Dehydrodeguelin separated as large yellow crystals. The residual organic material dispersed in the milky mother liquor was carefully decanted. The crystals were then washed with water by decantation, transferred to a filter and finally washed with methanol. The product was 5.4 g. of dehydrodeguelin, consisting of bright yellow pointed rods and needles whose melting point was 233°.

For preparative purposes dehydrodeguelin may be obtained by oxidizing crude

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[5] The optical data recorded in this communication were determined by George L. Keenan of the Food, Drug and Insecticide Administration of the U. S. Department of Agriculture. Appreciation is gratefully acknowledged for this valuable cooperation.

deguelin from derris. For example, 50 g. of crude deguelin in 10-g. portions gave by the above described procedure 19.6 g. of pure dehydrodeguelin, whose melting point was 233°. The material was recrystallized from a chloroform solution by adding 5 volumes of methanol. The melting point and appearance did not change. The crystals have straight extinction and negative elongation. The refractive indices are: η_α, 1.635 (shown lengthwise); η_β, 1.687 (shown crosswise) and η_γ, higher than 1.74.

Anal. Calcd. for $C_{23}H_{20}O_6$: C, 70.39; H, 5.14; OCH_3 (2), 15.8. Found: C, 70.20; H, 5.17; OCH_3, 15.8.

Several preparations of this compound had a melting point of 228°, which was not altered by repeated recrystallization. The analytical and optical data, nevertheless, were identical with those of the specimens melting at 233°.

Dehydrodeguelone.—Two grams of dehydrodeguelin dissolved in 30 cc. of boiling acetic acid was oxidized with 15 cc. of a 10% acetic acid solution of crystalline sodium dichromate (theory requires 10 cc.). After five minutes three volumes of methanol were added, immediately causing 0.26 g. of the oxidation product to separate. It consisted of bright yellow rods which melted at 287° (corr.).

This compound was recrystallized from its solution in chloroform by adding eight volumes of hot ethanol. The material separated as groups of bright yellow slender rods which began to contract and darken at about 280° and melt at 292° (corr.). It showed inclined extinction and negative elongation. Its indices of refraction were η_α, 1.505; the β value was not determinable and the maximum (γ) value was greater than the refractive index of methylene iodide (η_D, 1.74). However, many of the rods matched this liquid.

Anal. Calcd. for $C_{23}H_{18}O_7$: C, 67.96; H, 4.47; OCH_3 (2), 15.3. Found: C, 67.80; H, 4.58; OCH_3, 15.5.

Deguelic Acid.—To a 10% alcoholic solution of potassium hydroxide, made by adding 30 cc. of an aqueous solution of 15 g. of the alkali to 120 cc. of 95% ethanol, 5 g. of dehydrodeguelin and 10 g. of zinc dust were added, and the mixture was gently boiled for thirty minutes. After the zinc had settled, the clear liquid was decanted and cooled by adding crushed ice. The flask containing the zinc dust was washed with water, and the liquid was filtered from the zinc and added to the main reaction mixture, which was then diluted to 750 cc. The solution was made acid to congo red with sulfuric acid and extracted with ether. The ethereal solution was washed with water, dried with sodium sulfate, concentrated to 75 cc. and allowed to crystallize. The yield was 2.2 g. Upon allowing the mother liquor to evaporate a second crop of crystals was obtained, giving in all a yield of 53–55% of the starting material. The crude acid had a melting point of 183–185°. It was recrystallized by dissolving 1 g. in 20 cc. of boiling ethanol and adding an equal volume of water. The yield was 95%, and the substance had a melting point of 188°. A second recrystallization gave a colorless preparation whose melting point was 189° (corr.). It consisted of rods, square plates and needles. The extinction was inclined, and the sign of elongation was positive: η_α, 1.520; η_β, occurring infrequently, was 1.665; η_γ, >1.74. The most significant optical feature possessed by the substance, observed with convergent polarized light (crossed nicols), was the frequent occurrence of interference figures with the optic axis inclined. Many such crystals or fragments do not extinguish readily with crossed nicols (parallel polarized light) but remain bright when the microscope stage is rotated.

Anal. Calcd. for $C_{23}H_{24}O_8$: mol. wt. 428.3; C, 64.47; H, 5.65; OCH_3 (2), 14.5. Found: acid equivalent, 424; C, 64.32; H, 5.78; OCH_3, 14.7.

Dehydrodeguelin from Deguelic Acid.—A mixture of 0.25 g. of dry sodium acetate, 1 g. of deguelic acid and 4 cc. of acetic anhydride was refluxed for fifteen minutes. The condenser was then disconnected, and about 3 cc. of the liquid was removed by distillation and the residue carefully treated with methanol to decompose the remaining anhydride. Finally 15 cc. of methanol was added, causing the crystallization of 0.24 g. of brown rods, whose melting point was 228°. The material was purified by filtering its chloroform solution through norit, evaporating the filtrate to a small volume and adding 10 volumes of methanol. The substance separated as irregular-shaped salmon-colored plates and rods, which melted at 232°. Recrystallization of the compound in the same manner gave a product whose melting point was 233° (corr.). When this preparation was mixed with an authentic sample of dehydrodeguelin, the melting point was not depressed. Also, oxidation with chromic acid gave dehydrodeguelone. In spite of these facts and the fact that the analytical data given below were the same as those for dehydrodeguelin, the optical properties of the material were not the same as those recorded for this compound. However, when a specimen of the substance was dissolved in chloroform and the solution treated with several volumes of methanol in which a few crystals of pure dehydrodeguelin were suspended, the material separated possessed the optical properties recorded for dehydrodeguelin.

Anal. Found: C, 70.40; H, 5.27; OCH_3, 15.9.

Summary

1. The preparation, purification, and some properties of deguelin, a constituent of several tropical fish-poisoning plants, are described.

2. Evidence is presented to show that deguelin is a dimethoxylactone, $C_{23}H_{22}O_6$.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE NICHOLS LABORATORY, NEW YORK UNIVERSITY]

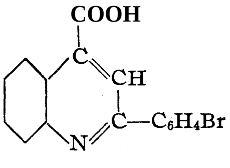
PREPARATION OF CERTAIN BROMINATED CINCHOPHENS

BY H. G. LINDWALL, J. BANDES AND I. WEINBERG

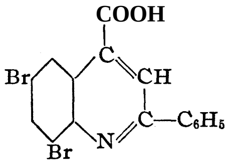
RECEIVED NOVEMBER 10, 1930 PUBLISHED JANUARY 12, 1931

It has been the purpose of this investigation to synthesize some brominated derivatives of cinchophen (2-phenylcinchoninic acid) in order to study later the physiological effects of the introduction of halogen. Condensations of 5,7-di-bromoisatin, as well as of isatin, with certain methyl ketones have been effected by means of the Pfitzinger[1] method.

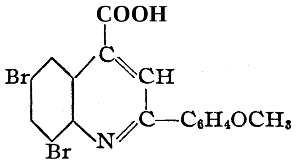
By the interaction of isatin and *p*-bromoacetophenone in the presence of potassium hydroxide in water and alcohol, 2-phenyl-4'-bromocinchoninic acid (I) was obtained. In the same manner, 5,7-dibromoisatin and acetophenone reacted to give 6,8-dibromo-2-phenylcinchoninic acid (11), while p-methoxyacetophenone and 5,7-dibromoisatin yielded 6,8-dibromo-2-phenyl-4'-methoxycinchoninic acid (III)



I



II



III

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[1] Pfitzinger, J. *prakt. Chem.*, 56, 292 (1897).

The non-halogenated derivative corresponding to (III) (4′-methoxy-2-phenylcinchoninic acid) was first prepared by Ciusa and Lazzatto[2] by Döbner's method.[3] This compound may also be prepared conveniently by the Pfitzinger method from isatin and *p*-methoxyacetophenone.

In the preparation of the 5,7-dibromoisatin it was found convenient to use a method described in the experimental part, employing 95% ethyl alcohol as a medium. This method has the advantage of speed as well as of good yield.

Experimental Part

5,7-Dibromoisatin.—Three grams of isatin and 40 cc. of 95% ethyl alcohol were heated on a steam-bath until the isatin was completely dissolved. While the solution was still hot, bromine (7.5 g.) was added slowly, drop by drop, with slow stirring of the mixture. The dibromo isatin began to separate from the mixture almost immediately upon the addition of the first few drops of bromine. After complete addition of bromine, the mixture was cooled slowly at first and later in ice. The product, after having been washed with water and with alcohol, was recrystallized from alcohol. 5,7-Dibromoisatin crystallizes from alcohol in long orange-red needles melting at 248–250°; yield, 80%.

Preparation of Substituted Cinchoninic Acids.—The procedure for the synthesis of 4'-bromo-2-phenylcinchoninic acid illustrates the general procedure A mixture of 15 g. of isatin, 22.5 g. of *p*-bromoacetophenone, 122 cc. of ethyl alcohol and 60 cc. of 33% potassium hydroxide solution was refluxed for eight hours with stirring. The alcohol was removed by distillation and the excess *p*-bromoacetophenone by steam distillation. The residual aqueous solution was cooled, acidified with hydrochloric acid and filtered. The solid was washed with water, followed by ethyl alcohol, and was crystallized twice from ethyl acetate.

These cinchoninic acids, pale yellow needles, are practically insoluble in water, ether, cold alcohol and cold ethyl acetate, but readily soluble in hot alcohol and hot ethyl acetate. The yield of recrystallized product is about 65% of the theoretical amount.

TABLE I

SUBSTITUTED CINCHONINIC ACIDS

Cinchoninic acid	Formula	Reactants	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Pound	Bromine, % Calcd.	Bromine, % Found
4'-Bromo-2-phenyl-	$C_{16}H_{10}O_2NBr$	Isatin and *p*-bromoacetophenone	239–340	4.27	4.18	24.36	24.00
6,8-Dibromo-2-phenyl-	$C_{16}H_9O_2NBr_2$	5,7-Dibromo-isatin and acetophenone	270–271	..	..	39.28	38.90
6,8-Dibromo-2-phenyl-4′-methoxy-	$C_{17}H_{11}O_3NBr_2$	5.7-Dibromo isatin and *p* methoxyacetophenone	263–264	..	..	36.58	36.00
2-Phenyl-4′-methoxy-	$C_{17}H_{13}O_3N$	Isatin and *p*-methoxyacetophenone	216	5.02	4.94	...	...

Summary

1. A convenient method of preparation of 5,7-dibromoisatin has been described.

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[2] Ciusa and Lazzatto, Gazz. chim. *ital.*, 44, [i] 64 (1914).

[3] Döbner, Ber., 20,277 (1887).

2. Isatin has been condensed with *p*-bromoacetophenone to yield 2-phenyl-4'-bromocinchoninic acid.

3. 5,7-Dibromoisatin has been condensed with acetophenone and with *p*-methoxyacetophenone to yield, respectively, 6,8-dibromo-2-phenylcinchoninic acid and 6,8-dibromo-2-phenyl-4'-methoxycinchoninic acid.

NEW YORK CITY

[CONTRIBUTION NO. 195 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

THE PREPARATION OF AROMATIC MERCURIC CHLORIDES FROM AROMATIC DIAZONIUM CHLORIDES

BY ROBERT E. MCCLURE AND ALEXANDER LOWY

RECEIVED NOVEMBER 14, 1930 PUBLISHED JANUARY 12, 1931

In an investigation[1] by the authors upon the electrochemical reduction of benzenediazonium chloride to phenylhydrazine hydrochloride it was noted that another substance was formed when the mercury cathode was violently stirred. This product proved to be phenylmercuric chloride. A non-electrolytic experiment showed that the formation of the latter compound was purely a chemical reaction and may be represented by the following

$$C_6H_5N_2Cl + Hg \longrightarrow C_6H_5HgCl + N_2$$

This reaction appears somewhat similar to the Gattermann reaction and suggests the possible formation of an unstable phenylcupric halide. The nature of the reaction also suggested that other aromatic mercury compounds might be prepared in the same way. Further investigation confirmed this point of view and this paper describes the preparation of a number of these compounds.

Nesmejanow[2] prepared a number of aromatic mercury halides by the reaction

$$\text{Aryl } N_2Cl{\cdot}HgCl_2 + 2Cu \longrightarrow \text{Aryl } HgCl + N_2 + 2CuCl$$

Experimental

It was evident in this type of reaction that the state of division of the mercury would be an important factor. A number of the usual types of stirrers were tried but even at high speed failed to give more than a small amount of the phenylmercuric chloride. An anchor-shaped stirrer, made from 4-mm. glass tubing with prongs drawn out to capillary fineness and with an opening at the base, gave good results. This stirrer was used in all the experiments described. The bottom of the stirrer was immersed in the mercury with the capillary tips extending into the solution. A fine spray of mercury was thrown from the tips by centrifugal action.

A **Typical** Experiment.—Five grams of redistilled aniline was dissolved in 30 cc. of concentrated hydrochloric acid and 50 cc. of water. The solution was cooled to 0°

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[1] McClure and Lowy, *Trans. Am. Electrochem. Soc.*, 56, 445–456 (1929).

[2] Nesmejanow, *Ber.*, **62B**, 1010 (1929).

and diazotized in the usual manner.[3] The diazotized solution was made up to 200 cc. volume with distilled water. A 1.5-cm. layer of mercury was placed in a GOO-cc. beaker and the solution added. The beaker was placed in an ice-bath and the temperature maintained below 5° throughout the entire experiment. The mercury and solution were stirred at 1000 r. p. m. Immediately after the stirrer was started a gray foam formed and gradually rose to the top of the beaker, persisting throughout the experiment. After four hours a test with alkaline β-naphthol showed that only a trace of the diazonium chloride remained. The stirring was stopped and the solution filtered through a Buchner funnel. The residue consisted of finely divided globules of mercury, which would not readily coalesce, and a fine grayish precipitate. The residue was boiled for several minutes with 100 *cc.* of water, which caused the mercury to coalesce. The precipitate was washed away from the mercury, filtered and dried by suction After drying, the residue was extracted with several portions of hot acetone, **300** cc. in all. After two recrystallizations 8 g. of white leaf-like crystals was obtained. This product readily sublimed to white leaflets, melting point 251°, which agrees with that given in the literature for phenylmercuric chloride.[4] The compound was further identified by treating with sodium iodide in cold acetone solution,[5] the phenylmercuric iodide resulting: melting point 265°.[6]

A number of aromatic mercuric chlorides have been prepared by the same type of reaction. The apparatus used and the procedure were as described in the typical experiment. The results are given in Table I.

TABLE I

RESULTS OF EXPERIMENTS

Amines diazotized, 6 g	**Product, -mercuric chloride**	**Solvent for purification**	Yield, g	Yield, %	**M** p , °C	M p.,[4] °C
Aniline	Phenyl-	Acetone	8	45	251	251
p-Toluidine	*p*-Tolyl-	Acetone	8	52	233	233 5
o-Toluidine	o-Tolyl-	Ethanol	11	72	146	146
2-Amino-1,4-dimethyl-benzene	2,5-Dimethylphenyl-	Ethanol	9	64	182.5	183
or-Naphthylamine	α-Naphthyl-	Benzene	2 5	**20**	188 5	189

Instead of using the mechanically divided mercury produced by stirring, black precipitated mercury was used. This was precipitated from mercuric chloride by stannous chloride and carefully washed until free of chlorides. This was rapidly stirred with the benzenediazonium chloride and a 20% yield of phenylmercuric chloride was obtained.

Further work is being conducted upon this reaction at the present time.

Summary

1. A method for the preparation of aromatic mercuric chlorides by the action of finely divided mercury upon the corresponding aromatic diazonium chloride has been developed.

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[3] Gattermann, Ludwig, "Practical Methods of Organic Chemistry," MacMillan Co., New York, **1927**, p. **237.**

[4] F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, **1921**, p. 172.

[5] Steinkopf, ***Ann.***, 413, 313, 329 (1517).

[6] F. C. Whitmore, Ref. 4, p. 174.

2. Phenylmercuric chloride, *o*- and *p*-tolylmercuric chlorides, 2,5-dimethylphenylmercuric chloride and a-naphthylmercuric chloride have been prepared by the above method.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SILICA GEL AS A CATALYST IN THE PREPARATION OF NITRILES[1]

BY JAMES A. MITCHELL[2] AND E. EMMET REID

RECEIVED NOVEMBER 14, 1930 PUBLISHED JANUARY 12, 1931

Previous investigations have shown that silica gel is an excellent catalyst for certain dehydrating reactions involving organic compounds. Milligan, Chappell and Reid[3] showed it to be an extraordinarily good esterification catalyst; Brown and Reid studied its application in the alkylation of ammonia and dehydration of alcohols[4] and also in the alkylation of aniline.[5]

The catalytic dehydration of the nascent amide formed from acetic acid and ammonia, according to the equation

$$CH_3COOH + NH_3 = CH_3CN + 2H_2O$$

in the presence of thoria and alumina, has been studied by Van Epps and Reid.[6] They found that an 85% yield of nitrile could be obtained at 500° with the better catalyst, alumina. They reported that no nitrile was obtained by passing ethyl acetate and ammonia over alumina, while Mailhe[7] obtained nitriles from esters and ammonia with both thoria and alumina.

This reaction has been investigated in the presence of silica gel.

Results

We have found that silica gel is a more efficient catalyst than either thoria or alumina in the preparation of nitriles from acids and ammonia. Using acetic acid and an excess of ammonia, as the temperature of operation is raised the percentage conversion to acetonitrile increases until at 500–525° a maximum is reached (practically quantitative). Increasing the temperature to 550° results in a decreased yield and increasing it to 575° lowers the yield still further. It appears that operation at tempera-

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[1] This and the two following papers, presented at the Atlanta meeting of the American Chemical Society, April, 1930, are extracted from a dissertation presented by James A. Mitchell to the Faculty of the Graduate School of Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Du Pont Fellow in Chemistry.

[3] Milligan, Chappell and Reid, J. *Phys. Chem*, 28, *872* (1924).

[4] Brown and Reid, *ibid.,* 28, 1067, 1077 (1924).

[5] Brown and Reid, THIS JOURNAL, 46, 1836 (1924).

[6] Van Epps and Reid, *ibid.,* 38, 2128 (1916).

[7] Mailhe, Bull. *soc. chim.,* [4] 23, 232 (1918); *Ann. chim.,* [9] *13,* **213** (1920).

tures above 500° fouls the catalyst, for after such treatment runs at lower temperatures gave low yields.

If the temperature of operation was not allowed to rise above 500° the catalyst was very slightly discolored and its activity continued unimpaired almost indefinitely, even after repeated heating and cooling in air.[8]

In every case when the temperature of operation was above 500° a noticeable quantity of a white solid formed in the condenser when distilling the lower (water) layer of the product. The higher the temperature the greater was the yield of this material. It was identified as ammonium carbonate. It is reasonable to suppose that even at temperatures of 500° or lower some ammonium carbonate is formed—which may account, in part, for the salting out of the nitrile to form the upper layer. The acetic acid not converted to nitrile or amide is, of course, in the lower layer in the form of ammonium acetate, and is also efficient as a salting out agent.

A rough calculation of the velocity of passage of the reactants through the catalyst in the case of acetonitrile shows that when the time of contact is twenty-five seconds at 500°, the percentage conversion is 95% (practically quantitative) and only 60% when the rate of flow of the reactants is twice as fast.

The results obtained show that highly purified gel and commercial gel are of the same order of activity.

All the aliphatic acids from acetic to heptoic, with an excess of ammonia, produce large yields of nitriles. The yield from lauric acid is decidedly lower and no nitrile has been obtained from palmitic acid. High yields of nitriles are also obtained from phenylacetic and hydrocinnamic acids.

With all the acids except acetic and isovaleric the catalyst blackens readily at temperatures of 500° or lower and loses its activity in most cases very gradually with use.

The yields of isovaleronitrile, above 90%, offer a rather surprising contrast with the yield of n-valeronitrile, which never exceeded 80%. The difference can hardly be ascribed to any difference in thermal stability of the two acids and, as the nitriles are relatively more stable than the acids, the results may indicate that the formation of nitrile from the isovaleric acid is much more rapid than from the normal acid.

In passing an ester with an excess of ammonia over silica gel the initial percentage conversion to nitrile is high, approximately the same as with the acid. The catalyst, however, in contrast with the acid reaction, is rapidly fouled. Aside from the greater instability of the ester as compared with the acid, the fouling of the catalyst might be partially explained by the decomposition products of the alcohol formed in the ester reaction.

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[8] With thoria and alumina the catalytic efficiency has been shown to fall off fairly rapidly with use.

Brown and Reid[9] have shown that large amounts of aldehyde are formed in passing butyl alcohol over silica gel. Our experience indicates that silica gel is rapidly fouled in any reaction involving the presence of aldehyde, probably due to the formation of polymerization products.

In passing ethyl benzoate and ammonia over silica gel, ammonium benzoate was obtained as one of the products of the reaction. In this instance we are dealing, after the initial reaction (1), with two competing reactions

$$C_6H_5COOC_2H_5 + NH_3 \rightleftharpoons C_6H_5CONH_2 + C_2H_5OH \qquad (1)$$

$$C_6H_5CONH_2 \rightleftharpoons C_6H_5CN\ 4\ H_2O \qquad (2)$$

$$C_6H_5CONH_2 + H_2O \rightleftharpoons C_6H_5COOH + NH_3 \qquad (3)$$

The fouling of the catalyst has been found to favor Reaction **3** (*i. e.*, more ammonium benzoate is formed) and decrease the yield of nitrile, Reaction 2. If the catalyst is effective in the establishment of both equilibria (2) and (3), it is only reasonable to expect that if it becomes less effective in one reaction it will also become less effective in the other. Two alternative explanations of the experimental result are possible: first, either the gel is such *an effective catalyst* for the establishment of equilibrium, **(3)** that partial fouling hardly impairs its activity, or, second, the hydration of the amide and dehydration of the ammonium salt, (3), is *independent of the catalyst* and merely involves a thermal equilibrium. As less amide is converted to the nitrile more is available for hydrolysis to the acid and ammonia.

In order to ascertain which of these two explanations is correct, benzamide was hydrolyzed in sealed tubes with and without silica gel. The gel had no effect on the rate of hydrolysis. Similar experiments using ammonium acetate showed that silica gel has no influence on the rate of formation of the amide.

It is evident, therefore, that silica gel affects only the second reaction, in the conversion of acids and ammonia to nitriles.

It is, of course, a well-known fact that ammonium salts of the aliphatic acids are easily dehydrated to the amide by the application of heat. Boehner and Andrews[10] and Boehner and Ward[11] have shown that various large-surface catalysts are active in the dehydration of amides. In our experiments in which amides were swept over silica gel by a current of air or nitrogen at temperatures above 400° very high yields of nitriles were obtained.

Experimental

Apparatus and Procedure.—The horizontal tube furnace used was similar to that described by Kramer and Reid.[12]

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[9] Brown and Reid, *J. Phys. Chem.*, 28, 1080 (1924).

[10] Boehner and Andrews, THIS JOURNAL, **38,** 2503 (1916).

[11] Boehner and Ward, ibid., **38,** *2505* (1916).

[12] Kramer and Reid, *ibid.*, 43, 880 (1921).

The catalyst, 100 g. of silica gel, was placed in a pyrex tube approximately 56 cm. by *23* mm. and activated by heating for four or five hours at 210° in a slow current of dried air, gradually raising the temperature to that desired in the experiment, while continuing the current of dried air.

An accurately measured quantity of acid (or ester) was passed through a dropping arrangement, the flow of which could be regulated by means of a glass rod ground in the tip, and introduced directly by a capillary into an atmosphere of ammonia, over the gel. The ammonia was passed through a calibrated flowmeter and led in through a separate tube ending a little short of the end of the capillary tube. An excess of ammonia was always used

The temperature was read from a thermometer placed between the catalyst tube and the wall of the furnace and kept constant within 1°. Temperatures above 500° were read with a thermocouple.

The gases after leaving the catalyst were led through a condenser, cooled by very cold water, and thence into a receiver, which in the case of acetonitrile was immersed in an ice–salt bath. The excess ammonia was allowed to escape.

The product invariably separated into two layers—the upper layer being practically pure nitrile and ammonia. The nitrile is salted out by ammonium acetate and ammonium carbonate. The lower layer in the case of the soluble nitriles also contained considerable nitrile.

Analysis.—Van Epps and Reid[6] estimated acetonitrile by fractional distillation. The product obtained, however, cannot be freed completely from ammonia, even after refluxing for some time.

The following analytical method proved very satisfactory. The two layers from the run were separated and distilled separately from a Claisen flask with an extended neck and the distillates collected up to 90°. The combined distillate from both layers was weighed and entered as product. The acetonitrile present was determined as follows. An accurately weighed sample of the product (about 0.5 g.) was sealed in a glass tube with *2* cc. of 18 N sulfuric acid and heated at 150° for two and one-half to three hours. The tube contents, after hydrolysis, were carefully washed into a *50-cc.* volumetric flask. A 5-cc. aliquot was titrated for total acidity with 0.1 N sodium hydroxide with phenolphthalein as an indicator, using throughout carbon dioxide-free water. A similar 5-cc. aliquot was heated in a porcelain dish on a water-bath for one and one-half hours, frequently washing down the sides of the dish with distilled water. The acetic acid formed by the hydrolysis of the nitrile was volatilized, leaving the excess sulfuric acid behind. The residue was titrated as before. The difference in the titers, of course, represents the acetic acid present—whence the acetonitrile in the product can be calculated. The estimation of propionitrile was effected in much the same manner. The two-layer product from the run was saturated with potassium carbonate. This effectively salted out the nitrile (an aqueous solution of propionitrile saturated with potassium carbonate retains in solution only about 0.02 g. per cc.). The upper layer was separated, distilled, and the fraction boiling between 90–98" analyzed as before.

Several similar analyses were run on butyronitrile, but this and the higher nitriles were easily purified and quickly freed of ammonia by distillation. Accordingly the higher nitriles were purified and estimated by fractional distillation.

Catalyst.—The catalyst used for the most part was ordinary 8–14 mesh commercial gel.[13] A purified gel catalyst was prepared by refluxing a sample of the commercial gel for several hours with concentrated nitric acid and subsequently cleaned by continued washing with distilled water until it was snow-white and acid free. A portion of the

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[13] Kindly furnished by Professor W. A. Patrick.

gel purified in this manner was further purified by electrolysis, until entirely freed of electrolyte.[14]

Materials.—The acetic acid was C. P. glacial acetic acid. The propionic, butyric and caproic[15] acids were technical materials carefully purified by distillation through a precision fractionating column. The isovaleric, lauric, palmitic and phenylacetic acids, butyl acetate and ethyl benzoate employed were the purest materials obtainable from the Eastman Kodak Company. The normal valeric acid used was prepared by the Grignard reaction from n-butyl bromide and carbon dioxide and purified by distillation through a fractionating column. Normal heptoic acid was prepared by oxidizing heptaldehyde with chromic acid mixture, separating the product formed and purifying by fractionation through a column.

Hydrocinnamic acid was prepared by completely reducing pure cinnamic acid with amalgamated zinc according to the method of Clemmensen[16] and recrystallizing the product from water until an accurate, sharp melting point was obtained.

n-Butyl n-butyrate was prepared by the oxidation and esterification of n-butyl alcohol with sulfuric–chromic acid.[17]

TABLE I

ACETONITRILE

Temp., °C.	Acid used, g.	Time of expt. min.	Rate of flow of ammonia, cc./min.	Product Amount, g.	Purity, %	Yield, %
		Effect of variation in temperature				
400	26.0	72	100	15.08	84	71
450	26.0	70	100	17.06	91	87
500	26.0	70	100	19.20	90	97
525	26.0	70	100	19.19	89	96
550	26.0	69	105	18.11	81	82
575	26.0	70	105	17.62	78	77
500	26.0	72	105	16.00	94	84
550	26.0	66	110	15.33	85	73
500	26.0	75	100	15.77	89	78
		Effect of variation in rate of flow				
500	26.0	74	110	18.13	85	87
500	26.0	80	150	17.60	79	78
500	26.0	71	180	17.44	81	79
500	26.0	105	150	14.28	92	74
500	26.0	30	230	11.83	89	60
500	26.0	89	105	18.43	85	88
500	26.0	110	100	20.30	87	98
500	26.0	100	80	19.58	83	91
		Gel purified by nitric acid and electrolysis				
500	31.0	77	105	21.07	92	92
500	26.0	75	110	19.37	84	91
500	26.0	75	110	17.37	89	87
500	26.0	72	105	17.27	93	90

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[14] Using the method described by O. G. Bennett, "Dissertation," Johns Hopkins University, 1930.

[15] Kindly furnished by Sharp and Dohme, Baltimore, Md.

[16] Clemmensen, *Ber.*, 46, 1837 (1913); 47, 51, 681 (1914).

[17] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 23.

The Preparation of Nitriles from Acids

Acetonitrile (Methyl Cyanide).—The effect of variation of temperature on the yield of nitrile is indicated in the first section of Table I.

Variation in the rate of flow of the two reactants was studied and the results are tabulated in Section II, Table I. Keeping the temperature constant at 500° it is evident, as is to be expected, that the time of contact with the catalyst is a factor of considerable importance. Increasing the rate of flow of either the acid or ammonia results in a decreased yield.

The results obtained in using a highly purified sample of the same gel are indicated in the third section of Table I. It is evident that similar yields of nitriles are obtained.

Each section of the table represents the results from a fresh charge of catalyst.

The two-layer product from the run was always water white without the least discoloration.

Propionitrile (Ethyl Cyanide).—The product, which always separated into two layers, was almost colorless, although several times a slight yellow coloration was apparent. After salting out with potassium carbonate, the upper layer upon distillation was quickly freed of ammonia and the boiling point rose rapidly to 95°. The fraction was taken between 90–98'—the major portion distilled between 95–97°. The propionitrile occasionally smelled faintly of ammonia, generally not at all, and the analyses showed a high degree of purity (98%).

TABLE II

PROPIONITRILE

Temp., °C.	Acid used, g.	Time of expt., min.	Rate of flow of ammonia, cc./min.	Product		Yield, %
				Amount, g.	Purity, %	
450	24.5	77	100	14.90	99	81
500	24.5	69	100	15.53	98	83
500	24.5	76	105	15.07	97	80
500	24.5	101	90	15.37	99	83
410	24.5	63	115	10.00	94	51
450	24.5	70	110	12.60	100	69
A new catalyst						
500	24.5	92	95	15.87	98	85
500	24.5	104	90	16.47	98	88
500	24.5	108	85	15.97	98	86

Lauronitrile (n-Undecyl Cyanide).—Ninety grams of lauric acid was passed over commercial gel at 500° with an excess of ammonia. The rate of flow was comparable with those of the other experiments. The acid was kept molten by surrounding the dropping apparatus with a "chimney," through which a current of hot air was passed. The temperature was kept constant (65°) to insure an even flow of acid.

TABLE III

HIGHER NITRILES

Temp., °C.	Acid used, g.	Time of expt., min.	Rate of flow of ammonia, cc./min.	Product, g.	Yield, %
		n-Butyronitrile			
450	23.7	65	100	15.24	82
500	23.7	105	100	17.57	94
500	23.7	68	100	17.00	91
500	26.0	113	90	19.00	93
450	23.7	63	110	14.37	77
500	23.7	71	110	16.37	88
500	23.7	84	80	16.88	90
		n-Valeronitrile			
500	44.0	134	95	27.10	76
500	22.0	92	80	14.40	80
500	22.0	105	80	14.60	81
510	22.0	80	90	13.00	73
		Isovaleronitrile			
500	23.0	75	90	16.9	90
500	23.0	89	95	17.3	92
500	23.0	114	85	17.7	94
500	23.0	84	85	17.4	93
		n-Capronitrile			
500	26.7	98	80	19.90	89
500	24.0	89	90	17.97	88
500	25.3	105	100	18.80	89
500	24.0	78	90	18.30	90
500	24.0	62	105	17.14	84
500	24.0	117	85	18.88	93
		n-Heptonitrile			
500	22.6	90	95	17.72	92
500	22.6	73	100	18.30	94
500	22.6	54	90	17.65	91
500	45.2	141	90	36.00	93

A fair amount of solid material was obtained in the product, which seemed to consist of the amide, and the ammonium salt of the acid.

The liquid product was washed with water and distilled under 98 mm. pressure. The larger part of the material distilled at 192–195°; yield of nitrile, 46.0 g. (55%).

Palmitic acid was passed over silica gel at 500° with an excess of ammonia. The acid was kept molten and at a temperature of 90°, using the same technique as with the lauric acid. The product was distilled under diminished pressure. The major portion distilled within 1.5 of 265° under 32 mm. pressure. It appeared to be a mixture of the amide and the acid. The product after several recrystallizations was still very impure and melted sluggishly around 40°. No noticeable amount of nitrile was obtained.

Phenylacetonitrile (Benzyl Cyanide).—One hundred and fifty grams of phenylacetic acid was passed over commercial gel at 500° with an excess of ammonia at a rate comparable to those in the previous experiments. The acid in the dropping arrangement was kept molten and at a temperature of 90° as before. The product separated into two layers. The upper (nitrile) layer was separated and distilled under vacuum. The product was almost pure nitrile. That fraction boiling between 128.5–129.5' at 31 mm. was entered as nitrile; yield, **112** g. (87%). The gel was completely blackened after use, but was still active.

Phenylpropionitrile (Phenylethyl Cyanide).—One hundred and twenty-three grams of hydrocinnamic acid was passed over commercial gel at 500° with an excess of ammonia, using the same technique as in the previous experiments with solid acids. The upper layer was distilled as before, practically all of it distilling at 141–142° at **25** mm.; yield of nitrile, 87 g. (81%).

The Preparation of Nitriles from Esters

Acetonitrile from n-Butyl Acetate.—The results obtained upon passing n-butyl acetate over commercial gel with an excess of ammonia are indicated in Table IV. Each space in the table indicates a change in catalyst.

TABLE IV

ACETONITRILE FROM n-BUTYL ACETATE

Temp., °C.	Ester used, g.	Time of expt., min.	Rate of flow of ammonia, cc./min.	Product		Yield, %
				Amount, g.	Purity, %	
500	21.8	64	95	9.64	70	87
444	21.8	47	100	9.80	65	82
400	21.8	77	95	10.50	59	80
400	21.8	81	90	10.22	46	61
370	45.3	129	90	11.17	59	41
404	43.6	112	90	12.17	47	37
370	43.6	120	90	12.00	52	40
400	43.6	120	85	14.57	52	49
455	43.6	112	95	15.82	61	63
465	43.6	123	105	14.60	55	52

The two layers of the product, highly colored and fluorescent, were separated and each distilled up to 85°. The material was analyzed for nitrile in the same manner as was the product obtained from acetic acid. At **500"** the efficiency of the catalyst decreased rapidly. At lower temperatures the life of the catalyst was longer, but its decline was still marked.

n-Butyronitrile from n-Butyl *n*-**Butyrate.**—Here again it is evident that good yields of nitrile are obtainable with a fresh catalyst, but the efficiency drops off rapidly with use (Table V, Section I).

Benzonitrile from Ethyl Benzoate.—As the use of benzoic acid was precluded by the type of apparatus employed, ethyl benzoate was passed over silica gel with an excess of ammonia gas. The formation of nitrile from the ester may be taken as sufficient indication that it is also obtainable from the acid. The results of experiments with ethyl benzoate are noted in Table V, Section II. It is apparent that favorable yields may be obtained. The catalyst, as with the other esters, is rapidly fouled.

The product invariably separated into two layers. The lower (nitrile) layer was distilled. The boiling point rapidly rose to 190° and practically all of the layer boiled between 190–195°. This fraction was taken as nitrile.

It was observed that during the experiments a considerable quantity of white solid collected in the condenser. As the catalyst was used and its efficiency decreased, the yield of this material increased. These crystals, upon examination, proved to be ammonium benzoate.

TABLE V

EXPERIMENTAL DATA

Temp., °C.	Ester used, g.	Time of expt., min.	Rate of flow of ammonia, cc./min.	Product, g.	Yield, %
		n-Butyronitrile from n-Butyl n-Butyrate			
380	43.4	96	90	11.00	53
410	45.1	122	85	12.50	58
450	43.4	123	80	13.51	65
500	43.4	102	95	15.49	75
450	43.4	113	80	11.70	56
		Benzonitrile from Ethyl Benzoate			
500	26.3		90	12.0	66
440	52 6	125	70	24.0	66
420	26.3	60	70	10.8	60
455	26.3	70	65	14.0	77
410	26.3	60	90	7.4	41
455	26.3	65	80	8.1	45

The Influence of Silica Gel on the Amide-Ammonium Salt Equilibrium.—Exactly weighed quantities of purified benzamide (0.3–0.4 g.) and a weighed quantity of water (about 1.1 g.—a large excess of water was used to force the hydrolysis of the amide) were sealed in pyrex tubes, half of the tubes containing about 0.5 g. of activated silica gel. Pairs of tubes with and without gel were heated at varying periods at 300'. The mixture of benzamide and ammonium benzoate was analyzed by the method outlined by Reid.[18] No difference was observed in the rate of hydrolysis of the amide, with or without gel.

Similar experiments were performed using ammonium acetate (at 150°). The rate of formation of acetamide was the same, with and without the gel.

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[18] Reid. *Am.* Chem. *J.*, 44, 76 (1910).

A solution of 100 g. of ammonium carbonate in 200 cc. of glacial acetic acid was divided into two equal portions, 5 g. of activated silica gel being added to one of them. These were refluxed side by side and at suitable intervals exact portions drawn off from each and analyzed. The rate of formation of amide was the same in both cases.

Summary

The formation of nitriles from acid or ester vapors mixed with an excess of ammonia in the presence of silica gel has been studied.

From the acids the following yields were obtained: methyl cyanide, 95%; ethyl cyanide, **85%;** n-propyl cyanide, 90%; n-butyl cyanide, 80%; isobutyl cyanide, 94%; n-pentyl cyanide, 90%; n-hexyl cyanide, 93%; *n*-undecyl cyanide, 55%; benzyl cyanide, 87%; phenylethyl cyanide, 81%. No cyanide was obtained from palmitic acid.

From the esters the following yields were obtained: methyl cyanide, 87%; n-propyl cyanide, 75%; phenyl cyanide, 77%.

The life of the catalyst is long in the case of the acids and short in the case of the esters.

The optimum operating temperature for the reaction is 500°.

The catalyst is only active in dehydrating amides, and is not effective in the establishment of the ammonia–acid, amide–water equilibrium.

Silica gel is by far the best catalyst for the reaction that has, as yet, been studied.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE DECOMPOSITION OF KETONES IN THE PRESENCE OF SILICA GEL

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RECEIVED NOVEMBER 14, 1930 PUBLISHED JANUARY 12, 1931

The decomposition of ketones in the presence of various dehydrating catalysts has been rather widely studied. Acetone has received the most attention, the condensation products being particularly well investigated.

Acetone kept for a long time over lime or aluminum chloride is transformed into mesityl oxide and phorone.[1] By passing acetone vapors over catalysts heated at a suitable temperature, thoria and alumina usually being employed, mesityl oxide, phorone, etc., have been obtained.[2] Ipatiew

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[1] Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 287.

[2] (a) Fittig, *Ann.*, 110, 23 (1859); (b) Beilstein and **Reith,** *ibid.*, 126, 245 (1863); (c) Paulow, *ibid.*, 188, 128 (1877); (d) Louise, Bull. *soc. chim.*, [2] **39,** 522 (1883); (e) Senderens, *ibid.*, [4] 3, 824 (1908); *Compt. rend.*, 146, 1212 (1908); (f) Mailhe and de Godon, Bull. *soc. chim.*, [4] **21, 63** (1917).

and Petrow[3] reported that mesitylene is the main product formed in heating acetone with dehydrating catalysts at high temperatures and pressures. Greene[4] produced hexamethylbenzene, hut no mesitylene, by heating acetone with zinc chloride. Reckleben and Scheiber[5] prepared hexamethylbenzene by leading a mixture of acetone and methyl alcohol over alumina at 400° and assumed that the mechanism of the reaction involved the intermediate formation of mesitylene. Contrary to this, Senderens[2e] reported that no mesitylene is formed from acetone with alumina.

Mesitylene, mesityl oxide, phorone, etc., are produced by distilling acetone with reagents such as sulfuric acid,[6] or boron trifluoride.[7] Heated with acetic anhydride, mesityl oxide is produced.[8] The formation of mesityl oxide is not confined to "dehydrating catalysts;" nickel, for example, yields this product.[9]

The gaseous products from the decomposition of acetone have received some little attention. With alumina Senderens[2e] reports the formation of a little gas at 400° which is an equal mixture of carbon dioxide and monoxide and ethylene. Adkins[1] says that "pure acetone passed over heated freshly prepared alumina forms condensation products, only about 60% of the acetone passing through unchanged. No gaseous products are formed." With copper–alumina at 650° Mailhe[10] obtained a gas containing 15% carbon monoxide, 30% methane and 55% hydrogen. Jacobsen[11] reported the formation of aromatic hydrocarbons, among them triethylbenzene, by treatment of methyl ethyl ketone with sulfuric acid but later work has shown that homologs of mesityl oxide and phorone only are produced by the catalytic condensation of methyl ethyl ketone.[12] Petrow[13] has shown that under conditions of high temperature and pressure homologs of mesityl oxide and isophorone are formed with only a trace of triethylbenzene.

Acetophenone condenses to s-triphenylbenzene in the presence of various catalytic agents at room temperature;[14] or simply by long refluxing.[15]

[3] Ipatiew and Petrow, *Ber.*, 59, 2035 (1926); 60, 735 (1927).

[4] Greene, *Bull. soc. chim.*, [2] 32, 422 (1879)

[5] Reckleben and Scheiber, *Ber.*, 46, 2363 (1913).

[6] See references given by Ekeley and Howe THIS JOURNAL, 45, 1917 (1923); also Orndorff and Young, Am. *Chem. J.*, 15, 249 (1893); "Organic Syntheses," John Wiley & Sons, Inc., New York, 1922, Vol. II p. 45.

[7] Gasselin, *Ann. chim.*, [7] 3, 58 (1894).

[8] Hoffman, THIS JOURNAL, 31, 722 (1909).

[9] Mailhe and de Godon, *Bull. soc. chim.*, [4] 21, 61 (1917).

[10] Mailhe, *Mat. Grass.*, 14, 6223, 6247 (1922); Bull. *soc. chim.*, [4] 31, 863 (1922).

[11] Jacobsen, *Ber.*, 7, 1435 (1874).

[12] Descude, *Ann. chim. phys.*, [7] 29, 494 (1913); Schramm, *Ber.*, **16,** 1681 (1883); Ekeley and Howe, THIS JOURNAL, 45,1917 (1923).

[13] Petrow, *Ber.*. 60, 2548 (1927).

[14] Engler and Berthold, *ibid.*, 7, 1123 (1874); Reddelien, *Ann.*, 388, 194, 173 (1912); *Ber.*, 46, 2717 (1913); Odell and Hines, THIS JOURNAL, 35, 82 (1913).

[15] Engler and Dengler, *Ber.*, 26, 1445 (1893).

Under conditions of high temperature and pressure, with alumina, triphenylbenzene, among numerous other materials, is produced.[16]

In the present investigation the decomposition of acetone, methyl ethyl ketone, and acetophenone has been studied in the presence of silica gel—particularly in connection with the condensation products formed.

Results

At atmospheric pressure and a temperature of 400–550° in the presence of silica gel the main condensation product of acetone is mesitylene, with a relatively small proportion of mesityl oxide, phorone, etc. At 500° a 17% yield of mesitylene is obtained. Silica gel seems to be the only dehydrating catalyst which in the gaseous phase converts acetone to mesitylene at ordinary pressures. Under conditions of high temperature and pressure silica gel also acts as an effective condensation catalyst. These conditions, however, favor the formation of high-boiling ketonic condensation products at the expense of low-boiling products including mesitylene. It is to be expected that high pressure would disfavor the mesitylene reaction since in this there is an increase in the number of molecules.

The method described here is advantageous for the preparation of mesitylene. The latter is readily isolated from the condensation product by washing with water and 70% alcohol, drying over calcium chloride and distilling, the fraction boiling between 130–190° being collected. The light-yellow oil thus obtained may be dried over sodium, which also effectively removes ketonic impurities, and subsequent fractionation yields a pure white oil of a high degree of purity.

The primary products in the homogeneous unimolecular decomposition of acetone are ketene and methane. The ketene then decomposes bimolecularly to ethylene and carbon monoxide.[17] In the presence of silica gel at 460° the highest percentage yield of ketene produced was 4.4%, 65% of the acetone used being decomposed. The gas evolved at this temperature contained 9% carbon monoxide, 17% methane, 28% carbon dioxide, 40% unsaturated hydrocarbon and 3% hydrogen. These facts show that the homogeneous decomposition of acetone in the presence of silica gel is taking place to only a minor extent at the temperature employed.

The presence of a small amount of methylacetylene in the gaseous products would indicate that the mechanism of the formation of mesitylene is dehydration of the acetone to methylacetylene and polymerization of the latter. Sabatier and Kubota[18] have assumed that the formation of mesitylene from allyl alcohol involves the intermediate formation of

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[16] Ipatiew and Petrow, *Ber.*, 60, 1956 (1927).

[17] Rice and Vollrath, *Proc. Nat. Acad. Sci.*, 15, 702 (1929).

[18] Sabatier and Kubota, *Compt. rend.*, 173, 17 (1921).

methylacetylene. The fact that acetone passed over magnesium powder at a red heat produces magnesium methylacetylide[19] shows that such a decomposition may occur.

Experiments so far, however, have not substantiated this deduction, for upon passing methylacetylene, produced from alcoholic potassium hydroxide and propylene bromide, over silica gel at temperatures between 400–500°, no mesitylene was isolated from the condensation product.

Methyl ethyl ketone does not condense to triethylbenzene in the presence of silica gel. Ketonic condensation products only are produced. This is in agreement with facts concerning the liquid phase condensation of the ketone—although sulfuric acid is effective in condensing acetone to mesitylene it will not convert methyl ethyl ketone to triethylbenzene. Furthermore, a comparison of the gaseous decomposition products of acetone and methyl ethyl ketone indicates that the two reactions are of a strikingly different nature.

Acetophenone, in the presence of silica gel, condenses in a manner similar to acetone, s-triphenylbenzene being formed.

Experimental

The apparatus employed was similar to that used in the work described in the preceding article.[20] The catalyst was 100 g. of activated silica gel.

Acetone Condensation Products.—An examination of the condensation product indicated that it consisted for the most part of water, unchanged acetone and mesitylene with small proportions of mesityl oxide, phorone, etc. An idea of the relative amounts of the constituents may be obtained by the results of a typical first fractionation (run at 430°): total condensation product 14 g.: 110–160°, 2 g.; 160–170°, 7 g.; 170–180°, 2 g.

The product from the acetone was washed with water, the upper layer separated, dried over calcium chloride, and distilled in a long-necked Claisen flask. The boiling point rose rapidly to 160° and the fraction boiling between 160 and 170° was taken as mesitylene.

The mesitylene was identified as the trinitro derivative.[21] Nitration of the fractions below and above 160–170° showed that they contained considerable mesitylene.

Although the mesitylene fraction was taken between a fairly wide range, ten degrees, the fact that the lower and higher fractions contained considerable of the hydrocarbon would indicate that it is not over-estimated—although, undoubtedly, the ten degree fraction is not pure mesitylene. The yields of mesitylene are indicated in Table I.

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[19] Keiser, *Am.* Chem. J., 18, 329 (1896).

[20] Mitchell and Reid, THIS JOURNAL, 53, 321 (1931).

[21] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1914, Vol. I, p. 201.

TABLE I

YIELDS OF MESITYLENE

Temp., °C.	Acetone used, g.	Rate of flow, cc./min.	Yield, g.	Yield, %
430	80	0.90	4.30	7.8
450	80	.75	6.65	12.0
500	40	...	3.82	13.9
500	40	.75	4.72	17.2
500	40	.75	3.40	12.4
500	120	1.00	10.40	12.6
500	120	0.75	11.71	14.2
500	80	.65	7.60	13.8
550	80	.75	6.59	11.9

Condensation products other than mesitylene were further fractionated and examined. The results are summarized in Table II.

TABLE II

OTHER CONDENSATION PRODUCTS

Fraction	Density, 25/25 Determined	Density, 25/25 Ipatiew and Petrow	Chief constituent	Density, 25/25 Pure compound
127–131°	0.828	0.828	Mesityl oxide	0.854
162–167°	.861	.857	Mesitylene	.862
192–200°	.891	.871	Phorone	.877
205–210°	.918	.896	Isophorone	.925
248–253°	.941	.922	Xylitone	$.936_4^{16}$

Mesityl oxide was further identified as the semicarbazone. Attempts to prepare the bromination product of the phorone (liquid) and the semicarbazone of the isophorone fractions were unsuccessful.

The mesitylene and xylitone fractions were only slightly soluble in 70% alcohol, while the others were readily soluble.

Experiments were performed under conditions of high temperature and pressure with silica gel, using the technique and equipment described by Herndon and Reid,[22] the products being treated as in the experiments at atmospheric pressure. The results of the first fractionation of the product obtained (50 cc. of acetone was heated for two hours with 5 g. of activated gel in bombs of 100-cc. capacity) are as follows

	At 350°, g.	At 400°, g.	At 350° without catalyst, g.
Acetone used	160	192	160
Fraction 100–160°	11	7	4
Fraction 160–170°	10	5	1
Fraction 170–220°	6	13	2
Residue	13	20	4

At 350° a small amount of gaseous products was formed.

[22] Herndon and Reid, THIS JOURNAL, 50, 3065 (1928).

Unchanged Acetone and Ketene.—Unchanged acetone and ketene were estimated as follows. A suitable aliquot of the aqueous condensation product, collected in two traps immersed in ice–salt baths and washed into a volumetric flask, was titrated with standard sodium hydroxide for acetic acid and from this the proportion of ketene calculated. Any ketene escaping the receivers was bubbled into a flask containing hot water (to decrease the solubility of the carbon dioxide) and estimated as before by titration. The unchanged acetone was determined by adding an excess of hydroxylamine hydrochloride to a second aliquot part and titrating the liberated hydrochloric acid with standard sodium hydroxide,[23] a correction being made for the acetic acid formed from the ketene.

TABLE III

EXPERIMENTAL DATA

Temp., °C.	*Acetone used,* g.	*Rate of flow,* cc./min.	*Ketene,* %	*Unchanged acetone*
470	3.95	0.66	2.3	19
500	3.95	.66	2.6	18
490	4.35	.66	2.0	15
500	**3.95**	.66	2.2	17
410	3.95	57	2.0	37
410	4.74	1.00	2.6	49
460	5.28	0.66	4.4	35
460	4.35	1.00	3.1	43
500	3.95	0.66	2.4	32
500	4.50	.80	2.5	30
500	3.95	1.25	2.1	52
500	3.96	0.66	2.6	33

Gaseous Products.—The gaseous products from the reaction were analyzed in an Orsat–Williams apparatus—the gases being collected over water saturated with the gas. Representative analyses of the gases produced are indicated in Table IV. Saturated hydrocarbon was calculated as methane.

TABLE IV

REPRESENTATIVE ANALYSES

Temp., °C.	*Acetone,* *g.*	*Rate of flow,* cc./min.	*Gas* evol., *cc.*	*Percentages*				
				CO_2	Unsat.	*CO*	H_2	CH_4
400	20.0	0.66	550	24.0	46.6	7.4	0	16.7
470	6.0	.66	400	28.0	40.0	9.2	3.2	17.0
450	8.0	.66	460	27.0	45.2	7.4	2.6	11.9
500	4.0	.66	350	26.8	44.7	7.5	3.0	
500	4.0	.66	400	25.0	43.5	8.7	2.7	

The presence of an acetylene hydrocarbon was thus shown: (1) a white precipitate was formed with mercuric sulfate acidified with sulfuric acid, (2) a cuprous salt was formed, soluble in ammoniacal ammonium chloride

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[23] Allen, "Commercial Organic **Analysis,**" 5th ed., 1923, Vol. I, p. 124.

(cuprous methylacetylide), (3) a silver salt was produced upon passing the gas through ammoniacal silver nitrate. The salts were decomposed by hydrochloric acid, evolving an unpleasant smelling gas.

Methyl Ethyl Ketone Condensation Products.—Upon passing the ketone over silica gel at 500° an oil insoluble in water, comparable in amount to that produced by acetone, was obtained.

From 140 g. of methyl ethyl ketone over 100 g. of commercial gel, at 500°, at the rate of 1.2 cc. per minute the following fractions were obtained: 110–145°, 1.9 g.; 145–160°, 1.2 g.; 160–170°, 0.8 g.; 170–210°, 1.6 g.; 210–220°, 1.5 g.; 220–300°, 4.9 g.; residue 5 g.

Heating 160 g. of the ketone in bombs, as in the acetone experiments, at 350° for two hours yielded the following fractions of condensation product, very little gas being formed: 110–150°, 1.2 g.; 150–170°, 8.5 g.; 170–205°, 7.5 g.; 205–225°, 3.5 g.; residue, 10 g. After further fractionation densities were determined:

Temp., °C.	Density 25/25 Determined	Density 25/25 Petrow	Chief constituent
160-167	0.854	0.8534	*Homo-mesityl oxide (peppermint-like odor)*
205-220	.877	.9048	*Homo-phorone*
238-248	.919	.9435	*Homo-isophorone*
260-270	.939	.9492[a]	*Homo-isophorone*

[a] Density 20/4, Ekeley and Howe.

Any triethylbenzene obtained would be in the second fraction. Repeated attempts to nitrate portions of this material with a mixture of equal parts of nitric and sulfuric acids (heating for twenty minutes) were futile. In a few cases a few crystals, too few to handle, were obtained. Unsuccessful attempts were made to nitrate all fractions of the product.

Most of the product was soluble in 70% alcohol, which also indicates that the product consists mostly of ketonic substances similar to mesityl oxide and phorone.

Unchanged methyl ethyl ketone was estimated as in the acetone experiments. The results at 500° using 3.94 g. of the ketone are summarized.

Time, min.	Ketone undecomposed	% Decomposition
18.5	1.29	67.2
16.0	1.27	67.6
17.0	1.39	64.7
17.5	1.34	66.1

Gaseous Products.—The results of the analyses of the gaseous products are indicated in Table V.

Acetophenone.—Passing 156 g. of acetophenone over 100 g. of commercial gel at 500°, at the rate of 0.5 cc. per minute, produced 12 g. of s-triphenylbenzene (9.8% yield).

The product from the acetophenone experiments was distilled directly

TABLE V

RESULTS OF ANALYSES

Temp., °C.	Ketone used, *g*	Rate of flow, *cc* /min.	Gas evol , *cc*	Percentages				
				CO_2	Unsat.	CO	H_2	CH4
500	4.05	0.66	275	15 5	15	12	2 2	30
500	405	.66	300	222	17.3	16.5		
				20.2	164			

until unchanged acetophenone was almost completely removed, The residue was washed with 90% alcohol, dissolved in benzene, filtered, the benzene removed by evaporation and the product taken up in ether. By spontaneous evaporation large, dark yellow crystals were obtained; these were removed while a good deal of mother liquor was still present, washed with dilute alcohol, and recrystallized from acetic acid. Several recrystallizations yielded a pure sample of triphenylbenzene, which was further identified as the monobromo derivative.

Upon heating acetophenone in the bombs at 350° a great variety of products was obtained. No triphenylbenzene was isolated from the viscous high-boiling fraction following the procedure previously described or after fractionation of the material under high vacuum.

Summary

1. The principal condensation product of acetone, in the presence of silica gel at 400–550°, is mesitylene. This is the only catalyst that has effected this reaction at atmospheric pressure. The yields of rnesitylene are comparable to those obtained by any other method.
2. It is suggested that the mechanism of the reaction involves dehydration of acetone to methylacetylene with subsequent polymerization of the latter to mesitylene. Experiments so far, however, have not substantiated this.
3. An analogous reaction does not take place with methyl ethyl ketone to an appreciable extent.
4. An analogous reaction takes place with acetophenone, yielding *s*-triphenylbenzene.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

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RECEIVED NOVEMBER 14, 1930 PUBLISHED JANUARY 12, 1931

The decomposition of acetic acid under the influence of various basic dehydrating catalysts has been well investigated, particularly in connection with the production of acetone, an excellent example of an "intermediate compound" catalytic reaction.

Chemically inert catalysts have been studied to some extent. Nef[1] observed that a high percentage of carbon monoxide was formed when acetic acid was passed over pumice at 500° and identified acetone as a minor product. Finely divided copper is also effective in converting acetic acid to acetone.[2] Senderens and Aboulenc,[3] upon passing acetic acid over charcoal, found that the gases produced contained 21.5% carbon dioxide and 35.5% carbon monoxide. The liquid product contained traces of ketone and aldehyde. Senderens[4] observed that when acetic acid was passed over precipitated silica, at 420°, among other materials, a gas was produced containing 90% carbon dioxide.

Kultashev and Kudryasheva[5] reported that over charcoal at 300° appreciable decomposition of acetic acid occurred, increasing with rise in temperature, acetone and methane being two of the products.

Results

In passing acetic acid over silica gel the maximum yield of acetone is obtained at 430–460° (about 29%). Above this temperature the increased amount of acetone decomposed more than offsets the increased amount of acetone formed. Above 400° appreciable decomposition of the acetone formed becomes noticeable. A small amount of an insoluble oil is obtained similar to that produced in the decomposition of pure acetone. Results are summarized in Table I.

In Experiments 19–24 aqueous acetic acid was used. It is evident that with aqueous acid a greater proportion of the decomposed acid is obtained as acetone. This would indicate that the proportion of water vapor present influences the rate of decomposition of the acetone—in accord with the results of Kultashev and Kudryasheva.[5] In Experiments 25–26 the same catalyst was used with glacial acetic acid.

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[1] Nef, *Ann.*, **318**, 221 (1901).

[2] Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 299.

[3] Senderens and Aboulenc, *Compt. rend.*, 170, 1064 (1920).

[4] Senderens, *Bull. soc. chim.*, [4] 3, 823 (1908).

[5] Kultashev and Kudryasheva, *Chem. Abstracts*, **19**, 2443 (1925); *J. Russ. Phys.-Chem. Soc.*, 55, 383 (1924).

TABLE I

EXPERIMENTAL RESULTS

Expt.	Catalyst	Temp., °C.	Time, min.	% Acid decomposed	% Yield acetone Based on acid used	% Yield acetone Based on acid decomposed
1	A	400	22	41.3	13.8	33.4
2		428	25	66.0	15.1	22.9
3		428	17	60.9	15.0	24.6
4		455	23	78.1	27.9	35.7
5		495	29	87.5	18.1	20.7
6		405	26	62.1	5.5	8.9
7		428	22	60.7	12.4	20.4
8		458	13	50.4	22.9	45.5
9		500	23	78.9	23.6	30.0
10	B	360	23	55.9	3.2	5.7
11		402	20	32.2	13.6	42.2
12		402	33	41.0	17.5	42.7
13		432	23	44.9	27.9	62.0
14		462	21	65.6	27.8	42.5
15		492	21	81.8	17.4	12.3
16		415	21	61.6	6.5	10.6
17		440	21	47.3	24.4	51.6
18		520	25	81.0	20.4	25.2
19	B	400	20	27.1	12.8	47.2
20		427	19	37.8	23.7	62.7
21	Using aqueous acetic acid	420	17	31.0	14.5	45.7
22		427	19	29.2	19.2	65.7
23		401	18	21.6	12.8	59.2
24		401	19	25.2	11.6	46.0
25		401	23	29.1	13.0	44.7
26		401	23	28.9	13.4	46.4
27	C	401	20	35.8	9.6	26.8
28		401	13	25.9	9.4	36.3
29		401	9	18.0	8.6	47.8
30		428	23	33.2	17.5	52.7
31		428	..	32.6	18.4	56.5
32	D	402	20	35.2	12.0	34.1
33		401	31	30.4	17.1	56.2
34		434	21	37.8	25.7	68.0

The acid used in each experiment was 5.114 g. Experiments 1–9, using commercial gel, catalyst **A,** cover a larger number of experiments and the last results therefore represent those obtained after considerable use of the catalyst. In Experiments 10–18 a fresh charge of commercial gel was used, catalyst B. In Experiments 19–24 aqueous acetic acid was used; 19 and 20 contained 4.0%; 21–23, 8.0%; 24, 2.0% water by weight. Experiments 25 and 26 were run on the same catalyst using glacial acetic acid. Experiments 27-31 were run on a sample of electrolytically purified gel after a short period of activation, namely, one hour at 200° and one hour at 450°, catalyst C. Experiments 32–34 were run on purified gel after the usual period of activation, catalyst D.

Purified gel and commercial gel are equally effective catalysts in the formation of acetone (Experiments 32–34).

Experiments 27–31, using gel activated for a short time, clearly indicate that the conditions of activation of the catalyst considerably influence its activity. Experiments 27–29 show that as the rate of passage of the acid is increased, although the actual yield of acetone is decreased, the yield based on the acid decomposed is increased—hurrying the material through the tube greatly decreases the amount of acetone decomposed.

The activity of the catalyst slowly decreased with use as appears from the results of Experiments 1–9, which cover a catalyst that had been used for quite a time. In this connection it is interesting to note that the gel is almost immediately blackened in this reaction, while in the nitrile reaction—using ammonia and acetic acid—at the same temperatures,[6] blackening of the gel takes place very slowly. The shining, jet-black gel is so completely impregnated with carbon that it cannot be burned out except on the outer surface at a red heat in a current of oxygen.

It is possible for acetic acid to decompose in two ways, in both of which carbon dioxide is produced

$$2CH_3COOH = CH_3COCH_3 + CO_2 + H_2O$$
$$CH_3COOH = CH_4 + CO_2$$

The results indicated in Table II, which involve the precise determination of carbon dioxide liberated in the reaction, clearly indicate that not all of the carbon dioxide liberated is obtained from the acetone reaction—some is obtained from the splitting of acetic acid into methane and carbon dioxide.

TABLE II

RESULTS OF EXPERIMENTS

No.	Catalyst	Temp., °C.	Weight of carbon dioxide, g.
1	A	400	0 880
2		450	1.116
3		450	1.206
4		450	1.161
5	B	500	1.508
6		500	1.130
7	C	300	0.000
8		350	.050
9		380	.386
10		400	.428
11	D	450	.580
12		500	1.285
13		500	1.046

Acetic acid (4.78 g. in each experiment) was passed over the gel at the rate of 0.2 cc. a minute. In order to make a correction for any carbon dioxide liberated in the decomposition of the acetone formed, blanks were run on pure acetone and the following corrections were subtracted from the amount of carbon dioxide found: at 400°, 0.024 g.; 450°, 0.044 g.; 500°, 0.054 g. The values given in the table are these corrected values.

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[6] Mitchell and Reid, **THIS JOURNAL**, 53, 321 (1931).

Experiment 6 was run after a large amount of acid (100 cc.) had been passed over the gel of Experiment 5.

Considering average results, a summary is made in the following table.

Temp., °C.	Acetone obtained, %	Methane produced if no acetone decomposed. %	HAc actually decomposed, %	Decomp. acid to acetone, %
400	14	18	37	65
450	28	19	65	85
500	24	28	81	90

The figures under "acetone obtained" are taken from Column 6 of Table I. Those in the next column are calculated from Table II by assuming that no acetone is decomposed after it has once been formed—the carbon dioxide corresponding to 14, 28 and 24% acetone being subtracted from the total carbon dioxide evolved, the remainder indicating the methane produced. It is evident that the sum of the figures of the second and third columns should equal the amount of acetic acid known to be decomposed, which was determined by titration (Table I). The difference between this sum and the acetic acid actually decomposed and the fact that the acetone reaction involves two molecules of acetic acid, whereas the methane reaction involves only one, makes it possible to estimate the amount of acetone decomposed under the conditions of the experiments and also, of course, the extent of the methane reaction.[7]

The conclusion is reached that 40 to 60% of the acetone originally formed in the reaction is decomposed—more, of course, being decomposed at the higher temperature. The acetone reaction is the predominant one. The estimate of the fraction of decomposed acid that is converted to acetone is given in the last column of the table.

This is in fair accord with the observation that acetone is decomposed to a similar extent in the presence of silica gel, using comparable rates of flow.

A comparison of the analyses of the gaseous products in the passage of acetic acid (Table 111), and acetone[8] over silica gel clearly indicates that the methane reaction is occurring to some extent—and the results agree in a general way with conclusions already deduced. Moreover, the analysis of the gases from acetic acid shows (1) that at lower temperatures the gas is richer in carbon dioxide (less acetone is decomposed), (2) that the amount of carbon dioxide evolved (and therefore acetone formed) decreases as the catalyst is used. Experiment 6, Table II, which was run on the

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[7] The decomposition into ketene and water would probably not occur to any great extent at these temperatures—Hurd and Martin, THIS JOURNAL, 51, 3614 (1929). Any attempt to estimate the extent of this reaction by isolating the ketene, or estimating acetic anhydride formed, would be meaningless as ketene is also formed from the decomposition of the acetone. In fact, it may not be unreasonable to suppose that the formation of acetone is the intermediate step in the decomposition of acetic acid to ketene.

[8] Mitchell and Reid, *ibid.*, 53, **330** (1931).

same catalyst as in 5, passing 100 cc. of acid between experiments, precisely confirms this observation.

TABLE III

EXPERIMENTAL DATA

Temp., °C.	Acid used, g.	Rate of flow cc./min.	Gas evol., cc.	Percentage of— CO_2	Unsat.	CO	O_2	H_2	CH_4
500	5.25	0.80	1700	47.5	7.5	9.0	2.0		
500	2.10	.80	600	42.5	7.0	22.5	0.5		
400	10.50	.80	150	52.2	2.6	18.4	1.8		
450	5.25	.80	450	50.5	4.5	22.1	0.5	2.2	20.2
500	2.10	.80	..	38.0	3.8	25.6	0.2	9.4	22.7
425	5.25	.56	175	63.0	8.5	6.5			20.0
460	3.15	.50	375	45.5	5.0	9.5			

Senderens' analysis[4] of the gaseous product obtained in passing acetic acid over precipitated silica, at 420°, indicated that it consisted of 90% carbon dioxide, and as the other 10%, consisting of carbon monoxide and a little ethylene, could be considered as decomposition products of the acetone produced, he concluded that the methane reaction did not occur.

The fact that silica gel, a chemically inert catalyst, is so effective in the conversion of acetic acid to acetone (85% of the acetic acid decomposed being converted into acetone) is hardly to be expected from the intermediate compound theory.

Experimental

The apparatus employed was similar to that described in the preceding article.[8] The catalyst, 100 g. of silica gel, was activated by heating for three hours at 210° and three hours at 450–500° in a slow current of air, dried with calcium chloride. A weighed quantity of the acid was passed through the dropping arrangement, through a capillary, and thence over the gel, through a condenser cooled by a rapid current of water and the product collected in a receiver immersed in carbon dioxide snow. An all-glass apparatus was employed—eliminating all rubber connections as well as "pockets" in which acid or product might be trapped. After passing the acetic acid over the catalyst the apparatus was swept out with nitrogen. The product was washed into a 50-cc. volumetric flask, a 2-cc. aliquot titrated for acetone by Messinger's method[9] and a 5-cc. aliquot titrated for unchanged acid with standard sodium hydroxide.

The exact determinations of carbon dioxide were made by passing the gases evolved from a weighed portion of acid through a condenser, an ice–salt trap, a small bubble tube containing water, a carbon dioxide snow–acetone trap, drying tubes and weighed soda-lime tubes. The tubes were brought to constant weight before and after the run, using a current of dried nitrogen.

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[9] Scott, "Standard Methods of Chemical Analysis," Vol. II, p. 1537, 1922.

The gas produced was analyzed in an Orsat–Williams apparatus, being collected over water previously saturated with the gas. The saturated hydrocarbon was calculated as methane.

Summary

The decomposition of acetic acid in the presence of silica gel at a temperature range of 400–500° has been studied.

Silica gel is an effective catalyst for the conversion of acetic acid to acetone. At least 85% of the acetic acid decomposed in the presence of silica gel produces acetone.

Baltimore, Maryland

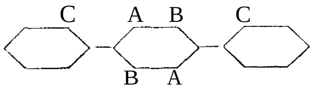
[Contribution from the Chemical Laboratory of the University of Illinois]

STEREOCHEMISTRY OF DIPHENYLBENZENES. MESO AND RACEMIC 2,5-DI-(3-BROMO-2,4,6-TRIMETHYLPHENYL)-3,6-DIBROMOHYDROQUINONES AND THE CORRESPONDING QUINONES. XII.[1]

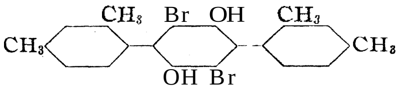
By P. R. Shildneck[2] and Roger Adams

Received November 17, 1930 Published January 12, 1931

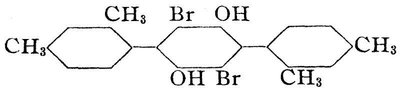
The possibility for the existence of a meso and a racemic modification of substituted 1,4-diphenylbenzenes of type (I) was demonstrated by isolation of two stereoisomeric 2,4-di-*m*-xylyl-3,6-dibromohydroquinones (IIa and IIb).[1b]



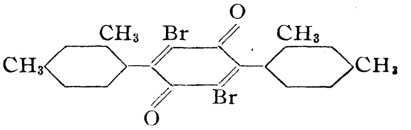
I



IIa



IIb



III

The two compounds formed two individual series of derivatives but oxidized to the same quinone (III). The quinone, in turn, upon reduction always gave a mixture of the two hydroquinones (IIa and IIb).

It was pointed out in the article describing these substances that on the basis of x-ray data and on the assumption that the quinone ring was essen-

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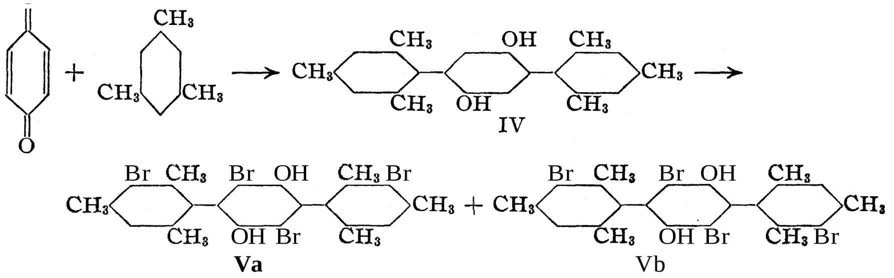
[1] The last three papers in this series are: (a) Stanley and Adams, This Journal, 52, 4471 (1930); (b) Steele and Adams, ibid., 52, 4528 (1930); (c) Browning and Adams, *ibid.*, 52, 4098 (1930).

[2] This communication is a portion of a thesis submitted by P. K. Shildneck in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

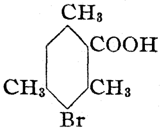
tially similar in character to the benzene ring, it might not be expected that two quinones would exist. The interference values indicated that in the quinone, although there would be collision between the methyl and the bromine groups, there would be none between the methyl and C=O groups and therefore free rotation would not be prevented.

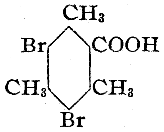
In this investigation the study of diphenylbenzenes has been extended in order to demonstrate that isomerism of this type is general. Compounds have been selected which have at each of the linkages of the benzene rings, the four ortho positions substituted. Under these conditions not only should two stereoisomers exist as found in the trisubstituted compounds but if the proper groups are present, x-ray data lead to the conclusion that two stereoisomeric quinones are possible. Results have fully substantiated these predictions.

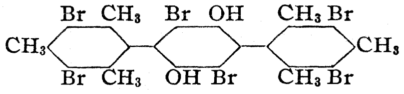
Mesitylene was added to *p*-benzoquinone and the resulting dimesitylhydroquinone (IV) was treated with four moles of bromine. Two isomeric tetrabromo compounds (Va and Vb) were readily isolated, each of which formed a characteristic diacetate. Although by the method of bromination (bromine in chloroform) it was very unlikely that two bromines could have entered a single mesitylene nucleus, nevertheless further information concerning the positions of the bromines in the two forms seemed desirable in order to be certain that two stereoisomeric compounds were in hand. Each of the two tetrabromo derivatives was oxidized with hydrogen peroxide and sodium hydroxide. There was formed first a deeply colored solution of quinone which gradually, after a long period of time, became nearly colorless. There was isolated as a result monobromomesitylcarboxylic acid (VI) in each instance. If the four bromines were not distributed with two in the inner ring and one in each of the outer rings in each molecule, part of the product should have been dibromomesitylcarboxylic acid (VII). No trace of this latter compound was found. Monobromomesitylcarboxylic acid and dibromomesitylcarboxylic acid were prepared by other methods and the latter was shown to be distinctly less soluble in water than the former. As a consequence the presence of any dibromo compound in a mixture of mono and dibromo should easily have been detected. The



monobromo compound, however, was essentially pure as received from the reaction mixture, though the yield was low, as might be expected from an oxidation reaction of this type.


VI

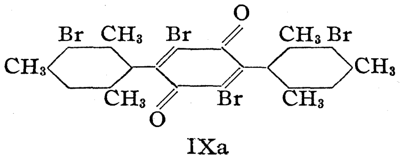

VII

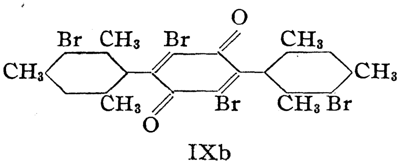

VIII

The two isomeric tetrabromohydroquinone derivatives (Va and Vb) upon treatment with liquid bromine yielded the same hexabromo derivative (VIII). This is of interest since it confirms the fact that the stereoisomers will exist only if each of the two end rings is asymmetrically substituted. The hexahromo derivative was then oxidized with hydrogen peroxide and sodium hydroxide. The reaction progressed in a fashion similar to the analogous oxidations of the two isomeric tetrabromo derivatives and pure dibromomesitylcarboxylic acid was isolated. Moreover, the hexabromo compound readily forms a diacetate and on oxidation the corresponding quinone.

All attempts to prepare the hexabromo derivative other than by the action of liquid bromine on the finely powdered tetrabromo derivatives failed. Likewise all attempts to prepare dibromomesitylcarboxylic acid by bromination of the monobromomesitylcarboxylic acid in solvents such as chloroform, carbon tetrachloride and glacial acetic acid failed. It was readily prepared by treating the solid monobromomesitylcarboxylic acid with liquid bromine. These facts indicate the unlikelihood of two bromines entering the mesitylene nucleus when the dimesitylhydroquinone was brominated in chloroform solution and further substantiate the contention that the two isomeric tetrabromo derivatives are stereoisomeric.

These two tetrabromodimesitylhydroquinones are of significance, not only because they represent a second example of stereoisomerism in the diphenylbenzene series, but because, unlike the two dibromodixylylhydroquinones which on oxidation give the same quinone, each upon oxidation yields an individual quinone (IXa and IXb). The two quinones differ from each other in solubility, melting point and other properties. The


IXa


IXb

two quinones are, in turn, readily reduced back quantitatively each to its respective hydroquinone (Va and Vb). These two quinones, therefore, represent the first instance in which isomerism of the diphenyl type has been discovered in molecules containing two rings one or the other of which is not a benzene nucleus. Which of the two quinones or hydroquinones is the meso and which the racemic is yet to be determined.

Experimental

2,5-Dimesitylhydroquinone (IV).[3]—In a 1-liter three-necked flask equipped with a mechanical stirrer and thermometer and surrounded with a freezing mixture of ice and salt was placed 700 cc of mesitylene (b. p. 164–168°). Stirring was started and when the temperature reached 0°, 150 g. of finely powdered anhydrous aluminum chloride was added at once. The suspension developed a deep red color.

Thirty grams of finely pulverized dry *p*-benzoquinone (purified by steam distillation) was added in 1-g. portions as rapidly as possible without permitting the temperature to rise above 5°. The well-stirred mixture became noticeably viscous and the original red color changed to brown. Stirring was continued for fifteen minutes longer and then 20 g. more of quinone was added as before, keeping the temperature below 5°. The mixture then became so viscous that continued stirring soon rolled up balls of brown gummy material in the excess mesitylene. Stirring was continued for three hours thereafter and then the flask with its contents was permitted to come slowly to room temperature overnight.

The excess mesitylene was decanted and the semi-solid residue decomposed in a mixture of 300 cc. of concentrated hydrochloric acid, 500 cc. of water and 500 g. of ice. The nearly white product was filtered with suction and washed with 3 N hydrochloric acid followed by hot water. The weight of air-dried crude product amounted to 40 g. Two crystallizations (with norite) from benzene gave 30 g. of pure white crystalline material melting at 225–226° (corr.).

The mesitylene was separated from the filtrate, combined with that previously decanted and steam distilled. In this way 600 cc. of pure mesitylene boiling at 164–168° was recovered. A residue of 45 g. of tarry material from the mesitylene and the mother liquors from the crystallizations yielded an additional 12 g. of pure material, making a total yield of 42 g.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.19; H, 7.57. Found: C, 82.97; H, 7.63.

Stereoisomeric **2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinones (Va)** and (Vb). Form (α).—In a 500-cc. three-necked flask equipped with a thermometer, reflux condenser and 250-cc. separatory funnel was placed 25 g. of 2,5-dimesitylhydroquinone and 75 cc. of chloroform. The mixture was heated to effect solution. The solution was allowed to cool to 50° and through the separatory funnel was then added a solution of 52 g. of bromine in 150 cc. of chloroform dropwise at such a rate that the temperature was maintained at 50–60°. At first the solution decolorized after each drop of bromine and heat was evolved. After about one-fourth of the bromine had been added the rate of absorption became slower and the temperature dropped. The reaction mixture was then gently refluxed and the remainder of the bromine added over a period of one hour. Refluxing was continued for one hour longer, during which time a heavy, crystalline precipitate appeared.

The reflux condenser was tilted dowuward and all but a few cc. of the chloroform distilled off; 250 cc. of fresh chloroform was added and distilled off as before, this time distilling to dryness on the steam-bath. The dry yellowish solid material in the flask was dissolved in 2 liters of acetone by refluxing for one-half hour. Then 2 g. of norite and 0.5 g. of powdered stannous chloride were added and refluxing was continued for

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[3] This compound was first made and analyzed by W. W. Moyer and described in his Ph.D. dissertation at the University of Illinois, June, 1929.

fifteen minutes longer. After a rapid filtration, the product separated on cooling. It was twice recrystallized from acetone, when it was obtained pure in the form of large rectangular prisms containing acetone of crystallization. The crystals effloresced to a white powder which when dry melted at 334–335° (corr.) with slight decomposition.

The filtrate from the original acetone crystallization was concentrated to 750 cc. and again cooled to room temperature. The crop of white prisms was filtered off (weight 2.5 g.) and the filtrate again concentrated to 250 cc. Upon cooling to room temperature and standing for several hours a third crop (1 g.) of white prisms was obtained. The two crops were combined and crystallized from 200 cc. of fresh acetone. About 2.8 g. of the α-form melting at 331–333° (corr.) was thus obtained.

Form (β).—The above filtrate of 250 cc. containing the more soluble material, was cooled to −10° in a freezing mixture. A white, fluffy precipitate appeared, quite different in appearance from the dense, granular less-soluble material. So soluble was this second material that it was found necessary to crystallize it from a mixture of acetone and water. For that purpose the acetone solution (250 cc.) was boiled for a few minutes with 1 g. of norite and 0.5 g. of powdered stannous chloride under the reflux, quickly filtered, heated again to boiling and hot water added a few cc. at a time until a permanent turbidity remained. Even from the hot solution a heavy precipitate of minute, shining flakes gradually appeared. The mixture was cooled to 0° and filtered. The crystalline precipitate was washed with 50% alcohol and dried. The yield amounted to 13 g. and the material melted at 292–294° (corr.).

The filtrate from this last crystallization was again heated to boiling and hot water added to the turbidity point as before. An additional 4.5 g. of product melting at 290–293° (corr.) was thus obtained. The last filtrate poured into an equal volume of water yielded 1.5 g. of less pure product.

The first two fractions were combined and recrystallized from a mixture of acetone and water as previously described, using, however. only 125 cc. of acetone. Thus 14.5 g. of pure material melting constant at 294–295° was obtained.

Wt. starting Material, g.	Less soluble product		More soluble product	
	Yield, g.	M. p., °C.	Yield, g.	M. p., °C.
25.0	27.5	334–335	17.5	294–295

Analysis of substance melting at 334–335°: a-form (Parr bomb). Calcd. for $C_{24}H_{22}O_2Br_4$: Br, 48.31. Found: Br, 48.16.

Analysis of substance melting at 294–295°: β-form (Parr bomb). Calcd. for $C_{24}H_{22}O_2Br_4$: Br, 48.31. Found: Br, 48.10.

The difference in solubility in acetone of the a-form and β-form is marked. A conservative estimate would place the ratio of solubilities in acetone at room temperature at fifty to one. There is also a similar difference in solubility in ethyl alcohol and toluene. Both of the forms crystallize from 95% ethyl alcohol in colorless flat prisms. From toluene the more soluble β-form crystallizes readily in long, slender needles, while the less soluble a-form dissolves with difficulty in boiling toluene and crystallizes with equal difficulty in very short needles.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone Diacetate (or-Form).—A solution of 5.0 g. of the higher-melting tetrabromohydroquinone (α-form) was made in 25 cc. of boiling pyridine. To this was added 25 cc. of acetic anhydride and the mixture was refluxed for thirty minutes. A white crystalline precipitate appeared during the refluxing. The mixture was then cooled, filtered, and washed with water. Upon purification from 85 cc. of pyridine a yield of 4.7 g. of small white prisms melting at 285–286° (corr.) without decomposition was obtained.

Anal. (Parr bomb). Calcd. for $C_{28}H_{26}O_4Br_4$: Br, 42.87. Found: Br, 42.70.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone Diacetate (β-Form).—This substance was made in the same way as the acetate of the a-form using **5** g. of the a-hydroquinone, **10** cc. of acetic anhydride and **5** cc. of boiling pyridine. Crystallization of the 5 g. of crude reaction product from 10 cc. of pyridine yielded a pure compound melting at 237–238° (corr.) without decomposition.

The solubility of this diacetate in boiling pyridine is from eight to ten times greater than that of the diacetate of the a-form.

Anal. (Parr bomb). Calcd. for $C_{28}H_{26}O_4Br_4$: Br, **42.87.** Found: Br, **42.81.**

Stereoisomeric **2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromoquinones (IXa)** and **(IXb).** a-Form.—A solution of **5.0** g. of the a-form of the hydroquinone in 1-liter of boiling 95% ethyl alcohol was treated with **5** g. of benzoquinone and the mixture refluxed for one-half hour. During this time the orange, crystalline a-quinone appeared. After distilling **750** cc. of alcohol from the reaction mixture on the steam-bath, it was cooled and filtered. The product was washed free of benzoquinone with two 15-cc. portions of cold ethyl alcohol and dried in air. The yield amounted to **4.6** g. of product which melted at 295–296° with decomposition. Recrystallization from toluene did not alter the melting point. The quinone was readily soluble in cold pyridine, moderately soluble in hot toluene, sparingly in boiling ethyl alcohol and insoluble in boiling methyl alcohol.

Anal. (Parr bomb). Calcd. for $C_{24}H_{20}O_2Br_4$: Br, **48.44,** Found: Br, **48.27.**

β-Form.—The oxidation was carried out in a manner similar to that of the a-form, except that for **5** g. of the lower-melting β-hydroquinone only **350** cc. of boiling **95%** ethyl alcohol and **5** g. of benzoquinone were used. About **200** cc. of alcohol was removed as the orange product crystallized. The yield was **4.6** g. and melted at 284–285° with decomposition. Recrystallization from toluene did not alter the melting point.

In appearance this quinone resembles the other. The two have approximately equal solubilities in toluene and both crystallize readily from that solvent in small orange prisms. **A** difference in solubility was found in ethyl alcohol, the β-quinone being the more soluble. Likewise in methyl alcohol the β-quinone was found sparingly soluble in boiling solvent whereas the a-quinone was practically insoluble in boiling methyl alcohol.

Anal. (Parr bomb). Calcd. for $C_{24}H_{20}O_2Br_4$: Br, **48.44.** Found: Br, **48.22.**

Reduction of a- and **β-Quinones.**—A solution of **2.0** g. of the a- or β-quinone in 10 cc. of boiling pyridine was treated with finely powdered stannous chloride until the pyridine solution became colorless. The reaction mixture was then thrown into excess of **3** *N* hydrochloric acid, warmed and filtered. The product was washed free of acid with water and air-dried. The yield was quantitative and amounted to **2.0** g.

The crude product from the α-quinone reduction was dissolved in **200** cc. of boiling acetone, filtered and concentrated to **100** cc. The solution was rapidly chilled in a freezing mixture and allowed to stand for one hour; **1.8** g. of a fine, white crystalline material was filtered off and air-dried. The substance melted at 334–335° (corr.) with slight decomposition and showed no depression in melting point when mixed with the original a-hydroquinone. The filtrate from the crystallization yielded about **0.2** g. of product which melted about **5** to **7°** lower.

The crude product from the β-quinone was recrystallized from acetone and water and gave white crystals melting at 294–295° with slight decomposition. **A** mixed melting point with the original β-hydroquinone showed no depression.

Oxidation of the a-Quinone with Hydrogen Peroxide and Sodium Hydroxide to **Monobromomesitylcarboxylic** Acid **(VI).**—The first step in the oxidation of the hydroquinones is the formation of quinones, consequently the complete oxidations were carried out with the quinones. To a solution of 6 0 g of the a-quinone in 250 cc. of 95% ethyl alcohol was added a cold solution of 50 g. of sodium hydroxide in 125 cc. of water. The mixture was stirred mechanically and 125 cc. of 30% hydrogen peroxide was slowly added. The flask was surrounded with running water to maintain the temperature at 10–20".

The quinone slowly went into a dark red solution, which changed to a light red in the course of six to eight hours. During the course of forty hours more the red color of the solution faded to a light pink and considerable sodium acetate crystallized out.

A cold solution of 25 g of sodium hydroxide in 50 cc. of water was added, plus 50 cc. more of 30% hydrogen peroxide and the reaction mixture stirred for twenty-four hours longer at room temperature. More sodium acetate crystallized out but the solution did not completely decolorize.

The sodium acetate was filtered off. To the filtrate was added 1 liter of water and an equal volume distilled off in order to remove the alcohol. The remaining pink solution was acidified with concd. hydrochloric acid. The mixture, which at this point contains a yellow flocculent precipitate, was diluted to a volume of 2 liters with water, boiled for a few minutes, then quickly filtered. From the clear colorless filtrate long silky needles appeared upon cooling. The filtrate was chilled to 0° and the white needles were filtered and dried. The yield amounted to 0 75 g. The crude product after three recrystallizations from water melted constantly at 168° (corr.).

Anal. (Parr bomb.) Calcd. for $C_{10}H_{11}O_2Br$: Br, 32.89. Found: Br, 32.81. Calcd. for $C_6H(CH_3)_3BrCOOH$: neut. equiv., 243. Found: 245.

Oxidation of the β-**Quinone** with Hydrogen Peroxide and Sodium Hydroxide to **Monobromomesitylcarboxylic Acid, (VI).**—Five grams of the β-quinone was oxidized in exactly the same manner as the α-quinone. The product was worked up in the same manner. There was isolated 0.80 g. of long silky needles which after three recrystallizations from water melted constantly at 168° (corr.). A mixed melting point with the acid obtained from the oxidation of the α-quinone showed no depression.

Anal. (Parr bomb). Calcd. for $C_{10}H_{11}O_2Br$: Br, 32.89. Found: Br, 33.02. Calcd. for $C_6H(CH_3)_3BrCOOH$: neut. equiv., 243. Found: 245.

Monobromomesitylcarboxylic Acid, **(VI).**—In a 1-liter, 3-necked flask equipped with a mercury-sealed mechanical stirrer, a dropping funnel and a reflux condenser, were placed 130.5 g. of mesitylcarboxylic acid,[4] 1 g. of iron filings and 250 cc. of carbon tetrachloride. One hundred thirty-five grams of bromine was placed in the dropping funnel, the stirrer started, the flask heated to an oil-bath temperature of 120–130°, and the bromine run in over a period of one-half hour. Stirring and heating were continued for an additional half hour, then the mixture was cooled and filtered. The product was treated with a solution of 200 cc. of hydrochloric acid in 300 cc. of water, again filtered, dissolved in an excess of 5% sodium hydroxide, filtered and the free acid obtained by acidifying this solution with hydrochloric acid. The product was recrystallized from carbon tetrachloride or better 50% alcohol and melted when pure at 168°. The yield was 112 g.

Anal. Calcd. for $C_{10}H_{11}O_2Br$: Br, 32.88. Found: Br, 32.40. Calcd. for $C_{10}H_{11}O_2Br$: neut. equiv., 243. Found: 244.

2,5-Di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone, (VIII).—Efforts were made to brominate further the ***a***- and β-forms of the tetrabromohydroquinones (Va) and (Vb) in chloroform, carbon tetrachloride and glacial acetic acid solutions without success. Liquid bromine gave the desired result?.

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[4] Made according to the method of Bamford and Simonsen, J. Chem. *Soc.*, 97, 1906 (1910).

(A) Bromination of the **α-Hydroquinone.—Five** grams of the finely powdered a-hydroquinone was placed in a 500-cc. Kjeldahl flask and 15 cc. of liquid bromine added. After standing for six hours the excess bromine was removed with air and the light yellow solid residue in the flask was washed with 5% sodium bisulfite solution, filtered and washed with water. The air-dried product (6.2 g.) was then dissolved in 60 cc. of hot pyridine and refluxed for a few minutes with 1 g. of norite and 0.25 g. of powdered stannous chloride. White granular crystalline material was obtained which was recrystallized from 50 cc. of fresh pyridine. The yield of product from this second crystallization amounted to 4.0 g. and the substance melted constantly at 395–398° (obs.) on the Bloc Maquenne.

Anal. (Parr bomb). Calcd. for $C_{24}H_{20}O_2Br_6$: Br, 58.51. Found: Br, 58.24.

(B) Bromination of the **β-Hydroquinone.—Five** grams of the β-hydroquinone was brominated in exactly the same manner as the α-hydroquinone. The reaction product was purified in the same way; 4.1 g. of purified product melting at 395–398° (obs.) on the Bloc Maquenne was obtained. A mixed melting point with the brominated a-hydroquinone showed no depression.

Anal. (Parr bomb). Calcd. for $C_{24}H_{20}O_2Br_6$: Br, 58.51. Found: Br, 58.19.

In order to make certain of no mistake, the bromination products of both the α- and @-hydroquinones were kept separate and converted independently to the diacetates and quinones. In each case identical products resulted.

2,5-Di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone **Diacetate.**—One gram of the hexabromo compound from the α- or β-tetrabromo compound was acetylated by refluxing with 10 cc. of pyridine and 10 cc. of acetic anhydride for thirty minutes. During the refluxing period the product crystallized from the boiling reaction solvent. The mixture was cooled and the crystalline precipitate filtered, washed with a few cc. of cold acetone and air-dried. The yield amounted to 1.05 g. After recrystallization from 15 cc. of boiling pyridine, 0.85 g. of pure white crystalline material melting sharply at 297° (corr.) was obtained.

Anal. (Parr bomb). Calcd. for $C_{28}H_{24}O_4Br_6$: Br, 53.06. Found: Br, 52.91.

2,5-Di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromoquinone.—One-half gram of the hexabromohydroquinone (produced either from the a- or β-tetrabromo compound) and 1250 cc. of 95% ethyl alcohol were refluxed until all was dissolved. Then 2.0 g. of benzoquinone was added, refluxing continued for one-half hour, and 1 liter of alcohol distilled off on the steam-bath.

The light orange-colored quinone crystallized during the distillation. The mixture remaining in the distilling flask was cooled and filtered. The product was washed free of benzoquinone with two 10-cc. portions of cold ethyl alcohol. The yield of air-dried product amounted to 0.48 g.

The quinone crystallized in the pure state from the alcohol reaction mixture and melted constantly at 390–393° (obs.) on the Bloc Maquenne. It was found to be soluble in hot pyridine and hot toluene and could be recrystallized readily from the latter.

Anal. (Parr bomb). Calcd. for $C_{24}H_{18}O_2Br_6$: Br, 58.64. Found: Br, 58.36.

Stannous chloride immediately decolorized the yellow pyridine solution, which after pouring into excess 3 N hydrochloric acid and crystallizing the white product from pyridine yielded the original hydroquinone melting at 395–398° on the Bloc Maquenne.

Oxidation of **2,5-Di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone** with Hydrogen Peroxide and Sodium Hydroxide to **Dibromomesitylcarboxylic** Acid, **(VII).—In** a 1-liter round-bottomed flask were placed 2.0 g. of the hexabromohydroquinone, 150 cc. of 95% ethyl alcohol and a cold solution of 20 g. of sodium hydroxide in 50 cc. of water. The mixture was stirred mechanically and immediately acquired a deep red color. After thirty minutes stirring, 100 cc. of water was added and the mixture stirred for two hours at 50°. It was then cooled to 20° and 50 cc. of 30% hydrogen peroxide stirred in. The flask was kept cooled to 10–20°.

Upon addition of the hydrogen peroxide the original dark red color of the mixture changed to a light red over a period of four to six hours. Stirring was continued at the same temperature for forty-eight hours. Sodium acetate crystallized out and the color of the reaction mixture changed to a pink. At this point a solution of 10 g. of sodium hydroxide in 25 cc. of water and 25 cc. more of 30% hydrogen peroxide were added

After an additional twenty-four hours of stirring at room temperature the sodium acetate was filtered from the pale pink solution and 500 cc. of water added to the filtrate. An equal volume (500 cc.) of water was distilled off to remove the excess ethyl alcohol. The residual solution was acidified with hydrochloric acid. The mixture, which at this point contained a yellowish flocculent precipitate, was diluted with water to a volume of 4 liters, brought to a boil and held there for a few minutes. It was then quickly filtered. Upon cooling the filtrate deposited a small crop of short white needles. The yield was 0.18 g. The melting point of this material, after recrystallization from 5 cc. of 50% ethyl alcohol, was constant at 210–211° (corr.). The yield was 0.11 g. of minute shining plates.

The substance was found to be soluble in 5% sodium bicarbonate solution, from which it was precipitated with hydrochloric acid as a white solid.

Anal. (Parr bomb). Calcd. for $C_{10}H_{10}O_2Br_2$: Br, 49.68. Found: Br, 49.50.

Dibromomesitylcarboxylic Acid, (VII).—In a test-tube 3.0 g. of monobromomesitvlcarboxvlic acid was treated with 5 cc. of liquid bromine at room temperature. The contents of the tube were then washed out with saturated sodium bisulfite solution and the collected light yellow solid residue washed with cold water. The yield of crude product amounted to 4.2 g. (air-dried).

The crude material was dissolved in 20 cc. of 95% ethyl alcohol and water added at the boil until a permanent turbidity appeared. Shining colorless plates appeared upon cooling. After one recrystallization from dilute (about 50%) ethyl alcohol the yield was 3.0 g of shining flakes melting constantly at 211° (corr.).

A mixed melting point with the acid obtained from the alkaline hydrogen peroxide oxidation of the hexabromohydroquinone showed no depression.

Anal. (Parr bomb). Calcd. for $C_{10}H_{10}O_2Br_2$: Br, 49.68. Found: Br, 49.83. Calcd. for $C_6(CH_3)_3Br_2COOH$: neut. equiv., 322. Found: 321.

Summary

1. Meso and racemic forms of 2,5-di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinones have been prepared. These were synthesized by brominating 2,5-dimesitylhydroquinone which in turn is readily formed by the addition of mesitylene to *p*-benzoquinone.

2. The two stereoisomeric compounds form characteristic diacetates and quinones. These latter compounds represent the first examples of the diphenyl type of isomers in compounds which have one of the rings not a benzene nucleus.

3. Each of the two 2,5-di-(3-bromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinones may be oxidized with hydrogen peroxide and sodium hydroxide to monobromomesitylcarboxylic acid,

4. The two hydroquinones may be brominated to the same hexabromo derivative, 2,5-di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone, thus indicating that symmetry in the end rings eliminates the stereoisomerism.

5. The hexabromo compound just mentioned forms a characteristic diacetate and quinone. Moreover, it is oxidized by sodium hydroxide and hydrogen peroxide to dibromomesitylcarboxylic acid.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NORTHWESTERN UNIVERSITY]

THE REACTJON BETWEEN CERTAIN ORGANIC SULFUR COMPOUNDS AND SODIUM IN LIQUID AMMONIA[1]

BY F. E. WILLIAMS WITH E. GEBAUER-FUELNEGG

RECEIVED NOVEMBER 17, 1930 PUBLISHED JANUARY 12, 1931

In connection with certain investigations on the sulfur compounds in crude untreated petroleum, it was found necessary to determine the effect of sodium on some simple organic sulfur compounds. Sulfides, disulfides and mercaptans were chosen for this study, since they are representative of divalent sulfur compounds which are supposed to exist in crude petroleum.

Very little work has been done on the effect of sodium on these types of sulfur compounds. Moses and Reid[2] found that organic sulfides are unattacked by sodium in ether even after standing for three months. Disulfides are converted into the corresponding mercaptans.

Kraus and White,[3] using a solution of sodium in liquid ammonia, converted diphenyl sulfide into benzene and sodium sulfide. No other reaction products were isolated. Apparently, the solution of sodium in liquid ammonia is more reactive than the ether–sodium system. We found this idea borne out in the present investigation.

With the three types of compounds studied, sulfides, disulfides and mercaptans, sodium might be expected to react in liquid ammonia, at least in two ways: first, it might carry the reduction to completion, yielding as

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[1] The investigation was carried out in 1928–1929 under a grant from the American Petroleum Institute, and specified as Project 17.

[2] Moses and Reid, THIS JOURNAL, 48, 776 (1926).

[3] Kraus and White, *ibid.*, 45, 775 (1923). We repeated Kraus' work on the reaction between diphenyl sulfide and sodium in liquid ammonia. Four experiments were made, two in which the procedure was identical with that described in the experimental part, and two in which the diphenyl sulfide was dropped into a solution of sodium in liquid ammonia as Kraus carried out the reaction. Our results were the same in all four experiments. A deep red solution was obtained when reaction was complete. The solid reaction product was a brown powder which ignited when exposed to moist air for a few minutes. Thiophenol and aniline were the only products identified. Benzene and sodium sulfide were watched for closely, since Kraus reported these, but we were unable to detect either compound.

final products sodium sulfide, hydrocarbons or amines or both; or second, the reduction might stop at an intermediate stage, forming sodium mercaptides, and hydrocarbons, or amines, or both.

So far as our present investigations show, only the second cotrrse is followed. Aliphatic sulfides are reduced to the corresponding mercaptides, and hydrocarbons, according to the equation

$$R_2S + 2Na + NH_3 = RSNa + NaNH_2 + RH$$

Disulfides are formed by oxidation of niercaptans. Treatment. with a reducing agent should reform the mercaptans. This was found to be the case as indicated by the general equation

$$R_2S_2 + 2Na = 2RSNa$$

Mercaptans, being weak acids, react with liquid ammonia to form slightly soluble, white crystalline ammonium mercaptides. If to a liquid ammonia solution of a mercaptide, sodium is added, the ammonium mercaptides are decomposed with the formation of sodium mercaptides, and the evolution of one-half mole of hydrogen

$$RSNH_4 + Na = RSNa + NH_3 + {}^1/_2\,H_2$$

Experimental

Materials.—The liquid ammonia was the regular commercial grade dried over sodium. The mercaptans, sulfides and disulfides were Eastman C. P. products.

Apparatus.—A new type of reaction chamber was designed for this investigation (see accompanying diagram). It was equipped with a mercury-sealed stirrer and connections for collecting gaseous reaction products.

Procedure.—Five grams of the compound under investigation was placed in the thoroughly dried reaction chamber, the stirrer placed in position and the two spiral exit tubes closed with two soda lime tubes. The reaction tube was then submerged slowly in the Dewar flask containing crude liquid ammonia. A stream of dried air was bubbled through the latter to cool it below the boiling point of liquid ammonia. One of the soda lime tubes was then removed and the exit tube of a small tank containing ammonia dried over sodium was connected by means of rubber tubing. A slow stream of gaseous ammonia was then run into the reaction chamber, where it condensed onto the sulfur compound and partially dissolved it. When 75 cc. of liquid ammonia had been condensed, the ammonia stream was stopped, but the connection allowed to stand. The remaining soda lime tube was then connected through a Bunsen valve to the gasometer.

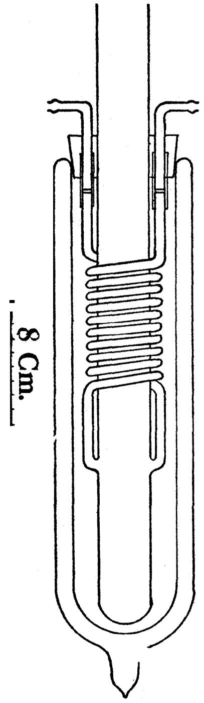

Fig. 1.

Stirring was then started, and clean sodium in the form of wire one-eighth inch in diameter and as long was dropped in, two pieces at a time. When the blue color had disappeared, another portion was added, and this was continued until the blue color remained permanent for two hours. At the end of this time the residual gaseous products were flushed into the gasometer with a fairly rapid stream of gaseous ammonia, the stirrer then quickly removed and the reaction chamber stoppered. Both exit tubes were connected to soda lime tubes and the reaction chamber set back into the Dewar flask from which the liquid ammonia had been removed. This precaution was necessary to prevent ebullition of the ammonia, which would force solid reaction products into the exit tubes. After about twelve hours, all of the ammonia had evaporated and a white crystalline product remained. This was scraped out, rapidly pulverized and preserved in a vacuum desiccator.

Sulfur was determined by oxidation with sodium peroxide in a Parr bomb and precipitated as barium sulfate.

Sodamide was determined by decomposing the sample with 10% sodium hydroxide solution, distilling the ammonia into standard acid as in the Kjeldahl method for nitrogen.

The gaseous products were analyzed by the conventional methods.

Aliphatic Sulfides

The reaction between n-propyl sulfide and n-heptyl sulfide and sodium in liquid ammonia was studied qualitatively with the following results: n-propyl sulfide yields n-propyl sodium mercaptide, sodamide and propane.

Normal heptyl sulfide crystallized when dropped into liquid ammonia and the solid appeared very insoluble. The reaction with sodium was very slow, but after fifty-five hours sufficient reaction had taken place to permit the identification of n-heptyl sodium mercaptide and sodamide. The amount of hydrocarbons produced was too small for identification and was mixed with unreacted organic sulfide.

Neither of these reactions produced a trace of sodium sulfide; the reaction always stopped with the formation of mercaptide.

Sodium sulfide was tested for in both alkaline and acid solutions. In the former case, a dilute sodium plumbite solution was mixed with a dilute solution of the solid reaction product. Not the slightest trace of black lead sulfide was produced.

To test for sodium sulfide in acid solution, a dilute solution of the solid reaction product, acidified with dilute hydrochloric acid, was treated with a few drops of lead acetate solution. No darkening of the solution or precipitation of black lead sulfide was noticeable.

Of a semi-quantitative nature was the study of the reaction between ethyl sulfide and sodium in liquid ammonia. The results of two representative runs are given in Table I. These values were calculated on the assumption of the ratio

$$1\ C_2H_5SNa:1\ NaNH_2:1\ C_2H_6$$

The yields of sodamide and ethane conform closely to the above ratio and suggest the following equation for the reaction

$$[C_2H_5]_2S + 2Na + NH_3 = C_2H_5SNa + NaNH_2 + C_2H_6$$

The ratio $C_2H_5SNa:NaNH_2$ 1 probably arises from a concomitant reaction

$$2\ [C_2H_5]_2S + 2Na = 2C_2H_5SNa + C_4H_{10}$$

Butane was not identified, however.

TABLE I

RESULTS OF REPRESENTATIVE RUNS

Run	Residue, g.	Wt. calcd., g.	Sulfur, %	Calcd. S, %	Extent of reaction
I	5.93	5.71	23.3	25.9	93.4
II	6.75	5.71	23.9	25.9	93.4

Run	Sodamide, %	Calcd., %	Extent of reaction
I	23.4	31.7	76.7
II	21.4	31.4	67.9

Run	Gas [N. T. P.], liters	Ethane, %	Found	Calcd.	Extent
I	1.04	79.1	0.83	1.04	79.1
II	0.99	72.3	0.71	1.04	69.6

Aliphatic Disulfides

The reaction between sodium and aliphatic disulfides in liquid ammonia was studied with ethyl, n-propyl and iso-amyl disulfides. The procedure was identical with that for the sulfides.

Qualitative examination of the reaction product showed that the alkyl sodium mercaptide was the only sulfur compound present, so the amount of mercaptide present was determined from the sulfur content of the solid product. The results for the three disulfides are tabulated in Table II.

TABLE II

Run	Residue, g.	Calcd. wt., g.	S, %	Calcd., %	Yield, %
		ETHYL DISULFIDE			
I	6.90	6.83	36.8	38.0	97.8
II	6.91	6.83	36.0	38.0	95.4
		n-PROPYL DISULFIDE			
I	6.47	6.20	31.9	32.6	102
II	6.38	6.20	32.0	32.6	102
		ISO-AMYL DISULFIDE			
I	5.85	5.55	24.0	25.4	99.5
II	5.93	5.55	23.8	25.4	99.9

Aliphatic Mercaptans

When mercaptans[4] are treated with liquid ammonia, slightly soluble white crystalline ammonium mercaptides are precipitated. When sodium is added to such a solution, a rapid reaction ensues with the formation of sodium mercaptides and the evolution of hydrogen, a reaction analogous to the reaction between ammonium bromide and sodium in liquid ammonia solutions.

$$NH_4Br + Na = NaBr + NH_3 + {}^1/_2\, H_2$$
$$RSNH_4 + Na = RSNa + NH_3 + {}^1/_2\, H_2$$

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[4] For the analogous reaction with thiophenols, see Ref. 3,

Summary

1. Aliphatic sulfides react with sodium in liquid ammonia chiefly according to the equation

$$R_2S + 2Na + NH_3 = RSNa + NaNH_2 + RH$$

2. Under the same conditions, aliphatic disulfides are reduced quantitatively to the corresponding mercaptides

$$R_2S_2 + 2Na = 2RSNa$$

3. Aliphatic mercaptans react as follows

$$RSH + NH3 = RSNH_4$$
$$RSNH_4 + Na = RSNa + NH_3 + {}^1/_2H_2$$

4. No sodium sulfide is produced in any of these reactions; the reaction stops with the formation of mercaptide.

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE OXIDATION OF "TRI-ISOBUTYLENE" BY OZONE

BY ROBERT J. McCUBBIN

RECEIVED NOVEMBER 24, 1930 PUBLISHED JANUARY 12, 1931

The preparation of the so-called tri-isobutylene was first described in detail by Butlerow,[1] who dissolved isobutylene in a cold mixture of five parts of sulfuric acid to one part of water. The resulting oil boiled at 177.5–179° (749 mm.) and had a specific gravity of 0.774 at 0°. Dichromate oxidation yielded carbon dioxide, trimethylacetic acid, acetic acid, an acid $C_{11}H_{22}O_2$, acetone, and a neutral oil. The acid $C_{11}H_{22}O_2$ distilled at 266° and melted at 66–70'. The neutral oil had a boiling range of 100–220°, reacted with phosphorus trichloride and sodium, but did not reduce Tollens' reagent. In order to explain the formation of the solid acid Butlerow assumed the structure of the hydrocarbon to be $[(CH_3)_3C]_2{=}C(CH_3)_2$. He stated that the oxidation might first involve a pinacolone rearrangement with the formation of $[(CH_3)_3C]_2C(CH_3)COCH_3$. Further oxidation of this compound would result in the production of $[(CH_3)_3C]_2C(CH_3)COOH$, which would account for a solid acid having the formula $C_{11}H_{22}O_2$.

In a recent communication[2] the author described the preparation of diisobutylene, the method of treating it with ozone, and the products resulting from the hydrolysis of the ozonide. In the work with tri-isobutylene a very similar procedure was followed.

Preparation of Tri-isobutylene.—Seven hundred fifty ml. of sulfuric acid and 250 ml. of water were mixed and cooled to about 5°. Then one liter of tertiary butyl

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[1] Butlerow, *Ber.*, 12, 1482 (1879).

[2] McCubbin and Adkins, THIS JOURNAL, 52, 2547 (1930).

alcohol was slowly added with constant shaking, care being taken to keep the temperature between 20 and 25'. The mixture was allowed to stand for about twelve hours and the oil layer removed. It was washed with dilute sodium hydroxide solution, dried over calcium chloride and fractionated twice over sodium, using a Widmer column. The yield of olefin, b. p. 175.5–179° (740 mm.), was 60-65%.

Formation and Hydrolysis of **Ozonide.**—Eighty-four grams (0.5 mole) of tri-isobutylene was placed in each reaction flask, using 100 ml. of glacial acetic acid containing 1.5–2.0% acetic anhydride as a solvent. The ozonization was carried out at 10°, the oxygen rate being 0.9–1.0 cu. ft. per hour. Under these conditions fifteen to eighteen hours sufficed for complete oxidation of 0.5 mole. The ozonide obtained from 1.5 or 2.0 moles of olefin was placed (with the acetic acid used as a solvent) in a 2-liter, three-necked flask equipped with a stirrer, a thermometer and an efficient reflux condenser. Stirring was commenced and about 5 ml. of water and 5 g. of zinc dust were added. Considerable heat was evolved and the flask had to be cooled. About 80 ml. of water and 60–70 g. of zinc were added over a two-hour period. The contents of the flask were allowed to warm up gradually to 50–60°, and when most of the zinc had reacted the flask was warmed until gentle refluxing took place. This was continued for at least an hour. Then enough water was added to dissolve most of the zinc acetate sludge and the oil layer was removed and dried over anhydrous magnesium sulfate.

After drying, the oil was fractionated up to 130". The remainder was washed free of acids with a solution of sodium bicarbonate. The water solution containing the sodium salts was saved and evaporated to dryness. The oil remaining was again dried and fractionated. The sodium salts just mentioned were distilled with phosphoric acid. Trimethylacetic acid was the only organic acid isolated, and it had resulted from the secondary oxidation of trimethylacetaldehyde, which was one of the principal scission products obtained from tri-isobutylene ozonide.

Hydrolysis Products.—In Table I are listed the principal fractions obtained from the hydrolysis of tri-isobutylene ozonide.

TABLE I

HYDROLYSIS PRODUCTS OF TRI-ISOBUTYLENE OZONIDE

Fraction	B. p., °C.	Formula	Yield, moles	Average yield
A	60–80	$(CH_3)_3CCHO$ (74°)	0.30–0 44	0.38
B	120–130	$(CH_3)_3CCH_2COCH_3$ (124°)	.20– .50	.40
C	180–190	$[(CH_3)_3CCH_2]_2C{=}O$ (182–185°)	.16– .23	.18
D	158–162 (23 mm.)	$[(CH_3)_3C]_2C(CH_3)COCH_3$	.1– .3	.16

Fraction A, trimethylacetaldehyde, was identified by means of the semicarbazone, m. p. 191". Fraction B was characterized as dimethyl-4,4-pentanone-2. Its semicarbazone melted at 176°.[2] Fraction C could not be obtained in a sufficient degree of purity to give consistent and conclusive analyses, but upon oxidation with dichromate two acids boiling at 164–165 and 177–182" were obtained. These acids were proved to be trimethylacetic and tertiary butylacetic by means of the amides, m. p. 153.5 and 131°, respectively. These facts indicate that this portion should have the structure assigned to it, although no ketonic derivatives could be obtained.

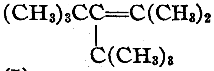
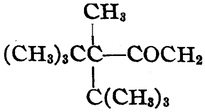
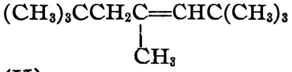
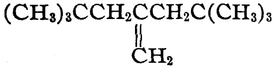
Fraction D also yielded no ketonic derivatives, but by further oxidation (dichromate) a solid acid (neut. eq. 186, b. p. 258–262°, m. p. 69–71°) was obtained. This corresponds to the acid obtained by Butlerow,[1] which he designated as methyldi-*tert.*-butylacetic acid.

In this table the amount of trimethylacetic acid obtained was calculated as trimethylacetaldehyde and it may be seen that the amounts of Fractions A and B are almost identical, indicating that these hydrolysis products are obtained from the same parent hydrocarbon.

In Table II are shown the hydrocarbons which would give rise to the above hydrolysis products of their ozonides.

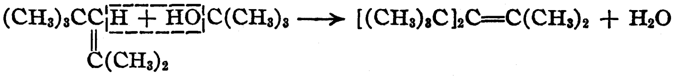
Table II

Structure of Isomeric Tri-isobutylenes

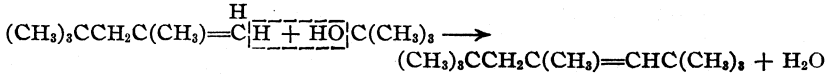
Hydrocarbon	Hydrolysis products
 $(CH_3)_3CC(C(CH_3)_3)=C(CH_3)_2$ (I)	 $(CH_3)_3CC(CH_3)(C(CH_3)_3)—COCH_3$
 $(CH_3)_3CCH_2C(CH_3)=CHC(CH_3)_3$ (II)	$(CH_3)_3CCH_2COCH_3$ and $(CH_3)_3CCHO$
 $(CH_3)_3CCH_2C(=CH_2)CH_2C(CH_3)_3$ (III)	$[(CH_3)_3CCH_2]_2CO$ and $HCHO \longrightarrow CO_2 + H_2O$

In order to obtain the ketone indicated from hydrocarbon number I it is necessary to assume that the pinacolone rearrangement suggested by Butlerow[1] has taken place during ozonolysis. Otherwise, acetone and hexamethylacetone, $[(CH_3)_3C]_2CO$, would be formed and no such products were obtained from this reaction.

In view of these facts, it is possible to assume that the formation of tri-isobutylene is actually a condensation involving the hydroxyl group of tertiary butyl alcohol and an hydrogen atom of di-isobutylene. Since the latter hydrocarbon exists in two isomeric forms, this mode of formation accounts for two forms of tri-isobutylene as follows

(I) 

$$(CH_3)_3C\underset{\displaystyle C(CH_3)_2}{\overset{}{C}}\boxed{H + HO}C(CH_3)_3 \longrightarrow [(CH_3)_3C]_2C{=}C(CH_3)_2 + H_2O$$

(II) 

$$(CH_3)_3CCH_2C(CH_3){=}\overset{H}{C}\boxed{H + HO}C(CH_3)_3 \longrightarrow (CH_3)_3CCH_2C(CH_3){=}CHC(CH_3)_3 + H_2O$$

Then a shifting of the double bond in the second hydrocarbon would produce a third isomer, *e. g.*

(III) $(CH_3)_3CCH_2C(CH_3){=}CHC(CH_3)_3 \longrightarrow [(CH_3)_3CCH_2]_2C{=}CH_2$

This theory is in accordance with the work of Lermontoff,[3] who synthesized di- and tri-isobutylene by saturating tertiary butyl iodide with isobutylene and heating this solution in a sealed tube with calcium oxide.

However, the above mechanism does not seem adequate to explain the formation of polymers when isobutylene is dissolved in cold concentrated sulfuric acid. The following formulas indicate a mode of formation which

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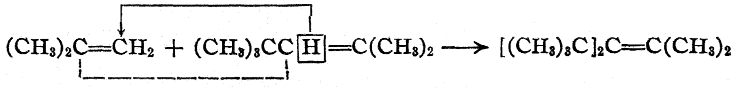
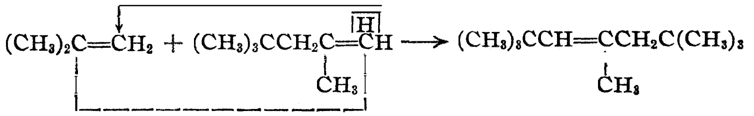
[3] Lermontoff. Ann.. 196, 116–122 (1879).

would produce the above olefins without requiring the presence of an alcohol or other derivative.

(IA) 

$(CH_3)_2C{=}CH_2 + (CH_3)_3CC\boxed{H}{=}C(CH_3)_2 \longrightarrow [(CH_3)_3C]_2C{=}C(CH_3)_2$

(IIA) 

$(CH_3)_2C{=}CH_2 + (CH_3)_3CCH_2\underset{CH_3}{C}{=}\overset{\boxed{H}}{C}H \longrightarrow (CH_3)_3CCH{=}\underset{CH_3}{C}CH_2C(CH_3)_3$

(IIIA) Same as III

Conclusions

From the data thus obtained, it appears that the hydrocarbon, known as tri-isobutylene, prepared by the action of sulfuric acid on tertiary butyl alcohol exists in at least three isomeric forms. These olefins are present in an approximate ratio of two moles of pentamethyl-2,2,4,6,6-heptene-3,4 (formula II) and one mole each of trimethyl-2,4,4-*tert.*-butyl-3-pentene-2,3 (formula I) and dimethyl-4,4-neopentyl-2-pentene-1,2 (formula III). It also seems apparent that during hydrolysis of the ozonide the hydrocarbon of formula I undergoes a pinacolone rearrangement instead of breaking down into two simple ketones.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CHLOROPHYLL SERIES. IV. THE DEGRADATION OF CHLOROPHYLL AND ALLOMERIZED CHLOROPHYLL TO SIMPLE CHLORINS

BY J. B. CONANT, J. F HYDE, W. W. MOYER AND E. M. DIETZ

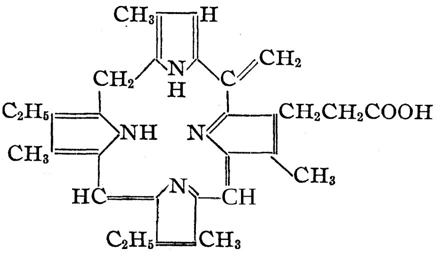
RECEIVED DECEMBER 8, 1930 PUBLISHED JANUARY 12, 1931

The thermal decomposition of chlorin *e* was described in the first paper of this series; the chief product of the reaction is pyrochlorin *e*, a monobasic acid whose spectrum resembles that of the parent compound. We have now studied this relatively simple chlorin in more detail and found that it is very closely related to phylloporphyrin. The ester of pyrochlorin e appears to be isomeric with the ester of phylloporphyrin, although the pyrochlorin *e* itself contains an additional molecule of water (a similar relationship between the hydrated free acid and the ester is found with chlorin e). By catalytic hydrogenation or reduction with hydrogen iodide by Fischer's method[1] and reoxidation, phylloporphyrin is formed in good yields. In the light of Fischer's recent syntheses,[2] phylloporphyrin appears to have one more carbon atom than was formerly supposed. This explains

[1] Fischer and Bäumler, Ann., 474, 65 (1929).

[2] Fischer and Helberger, *ibid.*, 480, 235 (1930).

why this porphyrin ($C_{32}H_{36}O_2N_4$) and pyrochlorin e have the same carbon skeleton although only two carbon atoms were eliminated from chlorin e ($C_{34}H_{38}O_7N_4$) in the pyrolysis. We suggest formula I for pyrochlorin *e;* the transformation to phylloporphyrin would involve the change of a methylene to a methyl group by virtue of a shift of hydrogen. This formulation corresponds to one of the two alternative formulas for phylloporphyrin suggested by Fischer.



I

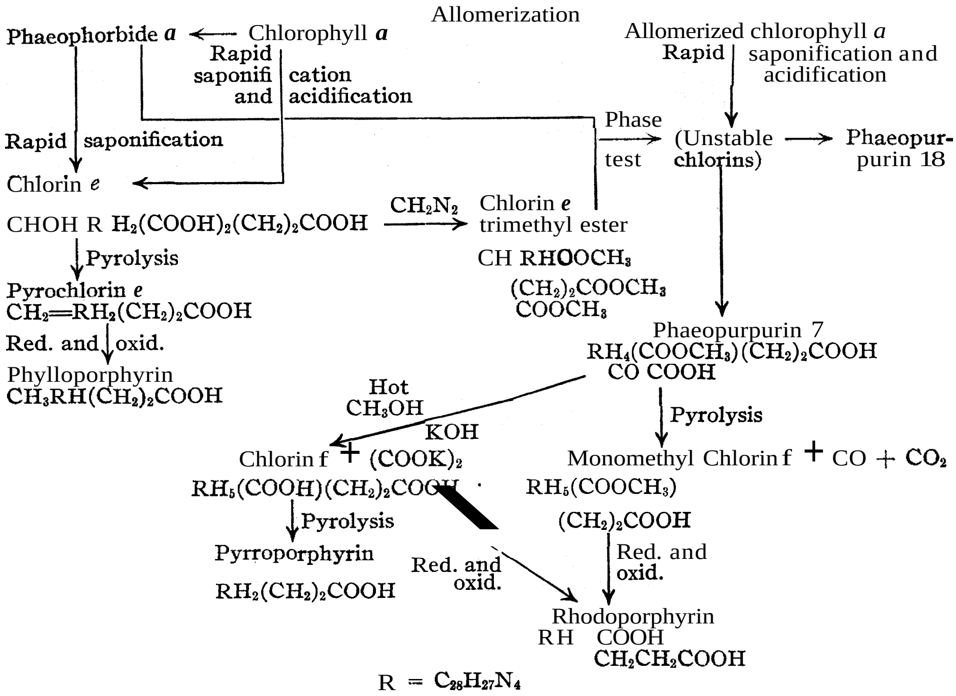
Pyrochlorin e may be considered as a normal degradation product of chlorophyll a since the relationship between chlorin e and the phaeophorbides was shown in the third paper to be closer than was at one time thought. (Both the phaeophorbides and the trimethyl ester of chlorin e give the phase test.)

After passing through the phase test the original structure of the chlorophyll molecule is in some way altered. This is apparent both from the failure of the products to give the phase test and from the fact that rhodoporphyrin or pyrroporphyrin and not phylloporphryin is obtained from them in the reactions which convert chlorins to porphyrins. We have now been able to show that phaeopurpurin 7, a characteristic product of the phase test, is formed by the rapid saponification of allomerized chlorophyll. Thus it is clear that the changes brought about by the phase test and allomerization are essentially the same as Willstatter pointed out. The degradation products of the phaeopurpurins are related to allomerized chlorophyll a, just as pyrochlorin e is related to unallomerized chlorophyll a.

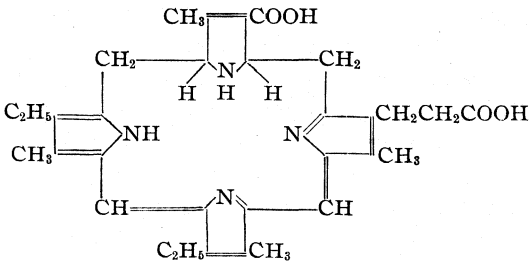
The degradation of both the "normal" and "allomerized series are outlined in the accompanying diagram. The decomposition of the phaeopurpurins, and the reactions of pyrochlorin e are here reported for the first time and the details are given in the experimental portion of this paper. The most satisfactory account of all these changes is indicated by the formulas given in the diagram. The symbol R is taken for $C_{28}H_{27}N_4$: thus, rhodoporphyrin is $RH{}^{COOH}_{CH_2CH_2COOH}$. The analyses of the compounds fit into this scheme as well as could be expected—it is, of course, impossible to be certain of a few hydrogen atoms. (The calculated values given in the experimental portion all correspond to the formulas given in this diagram.)

The following facts seem established by these transformations. (1) Allomerization and the phase test are equivalent and result in the change from a potential phylloporphyrin structure to a potential rhodoporphyrin and pyrroporphyrin structure. (The last part of this statement is implied in Willstatter's diagram if not explicitly expressed.) (2) The $=\underset{|}{C}-OCH_3$ group of methyl phaeophorbide is connected to the β-position of the pyrrole ring which in rhodoporphyrin holds the COOH group. This follows from the formation of rhodoporphyrin from monomethyl chlorin *f*, whose methoxyl group can be traced back to that of methyl phaeophorbide *a*. **(3)** Allomerization (phase test) changes the nature of one carbon atom of the chlorophyll skeleton so that it is easily eliminated together with carbon dioxide. Such elimination occurs in the change from phaeopurpurin 7 to chlorin f and monomethyl chlorin f. On the other hand, the same carbon atom is retained in the pyrolysis of chlorin *e* (unallomerized series).

It seems to us that the most satisfactory explanation of the phase test (allomerization) is to be found in the assumption that it is essentially an oxidation reaction involving the "extra" carbon atom. The transfer of hydrogen may be intra-molecular to a pyrrole ring or intermolecular to reduction products not yet isolated. The first explanation has been incorporated in the formulas given in our diagram.

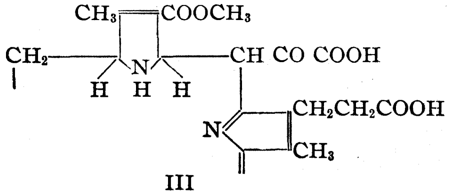


Chlorin f is the simple chlorin of the allomerized series; it differs essentially from pyrochlorin *e*, a simple chlorin of the unallomerized series, in that the extra carbon on the bridge has been eliminated. We suggest the following formula (II) for chlorin f:

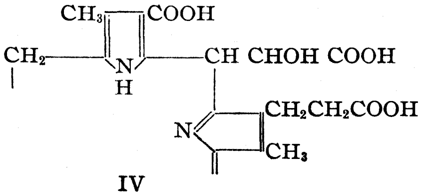


II

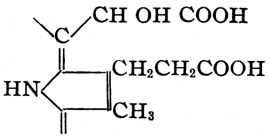
If the foregoing account is correct, the essential group in phaeopurpurin 7 is an a-keto acid on the bridge; this grouping has been suggested by Fischer as occurring in chlorin *e*. We have strong evidence for its presence (as shown in formula III) in phaeopurpurin 7, in that carbon monoxide is evolved in the pyrolysis and potassium oxalate is split off in the alkaline decomposition to chlorin f. For the corresponding compounds in the unallomerized series we might postulate such a grouping as that shown in IV, the change between the two being the internal oxidation and reduction previously referred to.



III



IV



V

This grouping could also take the form V (with or without lactone formation from the β-carboxyl); the presence of the linkage  $\mathrm{C{=}\underset{|}{C}{-}CHOHCOOH}$ would account for the ease with which chlorin e loses carbon dioxide without losing the "extra" carbon atom.

The nomenclature we have adopted warrants a word of explanation. The chlorin obtained from phaeopurpurin 7 by saponification is probably the same compound that Willstatter isolated from hydrolysis of altered chlorophyll; we have therefore retained this investigator's name for it; it is perhaps identical with the chlorin 10 of Treibs and Wiedemann.[3]

A number of interesting by-products were obtained in connection with the transformations outlined in the diagrams. In addition to pyrochlorin e there is formed in the pyrolysis of chlorin e a porphyrin which we designated as "pyrochlorin e porphyrin" in our first paper. After this was published Fischer and Moldenhauer[4] reported the preparation of a compound which they designated as chloroporphyrin e_3, from chlorin *e* by the action of hydrogen iodide. The absorption spectrum arid properties of this compound appeared to be identical with those of our pyrochlorin e porphyrin and this was confirmed by preparing some of Fischer's compound by his method and comparing'the two spectra in a Hartridge revision spectroscope. However, further study of our pyrochlorin e porphyrin convinced us that it was a mixture of phylloporphyrin with another porphyrin. We were able to separate this mixture by a long and tedious fractionation with hydrochloric acid. The chloroporphyrin e_3 was also resolved by the same method. The absorption spectrum of the new porphyrin which was thus separated from the admixed phylloporphyrin was distinctly different from phylloporphyrin and from that reported by us for pyrochlorin e porphyrin or by Fischer for chloroporphyrin e_3. However, on placing solutions of phylloporphyrin and the new porphyrin in two glass cells and passing a beam of light through both the resulting absorption spectrum was identical with that given for both our porphyrin and chloroporphyrin e_3. We propose to designate the porphyrin thus purified and freed of phylloporphyrin as pyrochloroporphyrin. Its analyses indicate that it is isomeric with phylloporphyrin.

In the conversion of the simple chlorins to porphyrins by means of reduction and oxidation, certain chlorins were formed which resembled in spectrum Fischer's synthetic chlorins. Thus, by the hydrogen iodide method we obtained from pyrochlorin *e*, a chlorin very similar to Fischer and Treib's phyllochlorin[3] which these investigators prepared from phylloporphyrin. A small but definite shift in one of the lines in the absorption spectrum and a difference of 15° in the melting point of the esters distinguishes our phyllochlorin from that of Fischer and Treibs. Some of the same phyllochlorin was obtained by catalytic hydrogenation and reoxidation of pyrochlorin *e;* this method was the most advantageous for the conversion to phylloporphyrin. The same phenomenon was met with in the allomerized series. In the conversion of chlorin f to rhodoporphyrin by means of hydrogen iodide, a chlorin was obtained in small amounts whose type of spectrum resembled the "synthetic" chlorins rather more than the parent chlorin or chlorin *e*. If the chlorin spectrum is characteristic of a partially

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[3] Treibs and Wiedemann, *Ann.*, 471, 146 (1929).

[4] Fischer and Moldenhauer, *ibid.*, 478, 54 (1930).

hydrogenated porphyrin (or its equivalent, see formula I for pyrochlorin *e)*, it is evident that many isomeric chlorins may be expected. From the pyrolysis of phaeopurpurin 7 we have also obtained two porphyrins in small amounts which appear to be new. The analysis of one of these (designated as porphyrin 8 in the experimental portion) indicates that it is isomeric with rhodoporphyrin monomethyl ester. The nature of this isomerism as well as that of pyrochloroporphyrin with phylloporphyrin (see above) remains to be explained.

The preparation of relatively large quantities of phaeopurpurin 7 and its dimethyl ester has been simplified by starting directly with phaeophytin a and b and putting this material through the phase test using as the reagent at room temperature a propyl alcoholic solution of potassium hydroxide. The unstable chlorins were treated with diazomethane, yielding dimethyl phaeopurpurin 7. From this by alkaline hydrolysis phaeopurpurin 7 may be obtained. As noted in the previous paper, it is particularly interesting that one methoxyl group is so much more resistant to alkaline hydrolysis than the other two. It was possible to prepare dimethyl phaeopurpurin 7 in the pure state without first separating the *a* and b series by virtue of the fact that in the b series the products of the phase test are rhodins *i* and k, which Willstatter showed to be relatively stable; they are not transformed by treating with diazomethane. Starting with pure methyl phaeophorbide b we found that there was no substance formed with acid number corresponding to dimethyl phaeopurpurin 7. In this new procedure from phaeophytin *a* and b all the b series is lost, but, in spite of this, because of the great saving in labor, this is very much the best method of preparing the compound.

Experimental

Pyrochlorin e.—The preparation of this compound has been improved by using boiling diphenyl and a shorter time of heating. A typical procedure is as follows: a 100-g. portion of diphenyl was heated to boiling over a free flame and 1 g. of chlorin *e* was then quickly added and the boiling continued for five minutes with vigorous shaking. On adding the chlorin there was a short, but vigorous, evolution of gas. The hot reaction mixture was then poured cautiously into a liter of ether in a two-liter flask. The reddish-brown ether solution thus obtained was extracted repeatedly (about 10 times) with 200-cc. portions of 1% hydrochloric acid until the color was very light, each fraction being washed twice to remove diphenyl. These extracts were retransferred to about 2 liters of ether. The ether solution of the 1% acid extract was re-extracted with 0.5% hydrochloric acid. This retreatment leaves the impurity with the red line at 650 mp in the ether. The "pyrochlorin e porphyrin" was transferred to 2 liters of ether from which it crystallized in prismatic needles as usual on evaporating the solution to 100 cc. In this way from two 1-gram runs 250 mg. of porphyrin was obtained, which represents a 15% yield. The combined mother liquors from the two runs containing the pyrochlorin e were then worked up in the usual way and yielded 0.615 g. of pyrochlorin e, which is a 36% yield.

Anal. Calcd. for $C_{32}H_{38}O_3N_4$ ($C_{32}H_{36}O_2N_4 \cdot H_2O$): C, 73.0; H, 7.22; N, 10.65. Found: *C*, 74.1, 74.3, 74.5; H, 7.0, 7.4, 7.5; N, 10.3, 10.4.

The spectrum in ether has been published (paper I). The spectrum in 8% hydrochloric acid was as follows: 1, 672.7---669.2—628.1---625.0; II, 613.5—592.4; III, 563.4---541.8---525 2; E. A. 442.2. Order of intensity: I, III, II.

Methyl Ester of Pyrochlorin e.—The pyrochlorin e was methylated in ether solution with diazomrthane. The ester crystallizes only after concentrating the ether solution to a very small volume and diluting with ethyl alcohol. It comes out in beautiful, almost perfectly equilateral, triangles of bright luster; it melted sharply at 184". The spectrum was identical line for line in a revision spectroscope with the spectrum of the parent substance.

Spectrum of Pyrochlorin e Ester in Ether.—Concn. 0 2 g./5 liters at 65 mm. depth: I, 677.1—637.1---627.4; II, 614.5---610.3—595.8---594.2; III, 595.5-"-548.2 (hazy); IV, 534.3---532.5---525 5; V, 517 9---516.2480.7; E. A.441.8. Order: I, V, II, IV, III.

In 10% Hydrochloric Acid.—I, 674.8---672.6---626.4; II, 614.2—595 6---590.0; III, 563.9---550---543.5---525.9; E. A. 444.1. Order: I, III, II.

Anal. Calcd. for $C_{33}H_{38}O_2N_4$: C, 75.85; H, 7.28; N, 10.73; OCH_3, 5.94. Found: C, 75.5, 75.7; H, 7 2, 7.8; N, 10.6, 10.7; OCH_3, 5.7, 6.2.

The statement in our previous paper that pyrochlorin e was unstable has not been verified. Carefully purified material, even after long standing, has been found to be unchanged. A solution of pyrochlorin e ester in glacial acetic acid was boiled for twenty-four hours without apparent change. No other product could be found. Decomposition with potassium hydroxide (alcoholic) and pyridine at 220° for five hours yielded phylloporphyrin, identified by mixed melting point of the esters. The copper, zinc and iron salts were made by heating pyrochlorin e ester with the corresponding acetates in glacial acetic acid. The only one of these which could be obtained in nicely crystalline condition was the copper salt.

The copper compound dissolved in ether with a deep blue-green color from which it was not extracted by strong acid and showed the following spectrum: I, 648.7---646.0--609.8---606.9; II, 589.1---576.2; III, 550.5---532.3; IV, 613.8—493.7; E. A. 434.5. Order: I, IV, II, III.

Anal. Calcd. for $C_{33}H_{36}O_2N_4Cu$: C, 67.9; H, 6.16; N, 9.6; OCH_3, 5.3; Cu, 1.09. Found: C, 66.6, 68.3; H, 6.4, 6.7; N, 9.3; OCH_3, 4.7; Cu, 1.01, 1.05.

The iron salt gave a deep green ether solution, from which it was not extracted with concentrated hydrochloric acid. Its ether solution behaved in a peculiar way in that when shaken with dilute ammonia the color became brown and the spectrum was altered considerably. On shaking with acid the original color and spectrum returned. Dilute potassium hydroxide does not appear to effect the same change. The initial spectrum in ether was: I, 671.4—646.1---644.1; II, 619.2---617.1-600.3---596.1; III, 564---545.8 (very faint); IV, 533.1—526.2; V, 513.3---509.0499.6---497.2—487.5 (double max.); E. A. 444.9. Order: I, V, 11, IV, 111.

The spectrum after treatment with ammonia was as follows: I, 690.7---673.4—646.6---644.6; II, 532.4---526.8; III, 513.6---508.4—500.0—49F488.5; E. A. 452. Order: I, 111, 11.

The color of the zinc complex in ether was pure blue. It was readily attacked by 10 or 15% hydrochloric acid, which extracted it with a pure green color. Its spectrum in ether was: I, 672.0---669.3—641.8; II, 634.2---633.3-622.3---620.0; III, 603.6---591.0; IV, 557.8---544.5; V, 534.1—525.1; VI, 517.3---512.9—487.6 (hazy); E. A. 446.6. Order: I, II, VI, III, V, IV.

Catalytic Hydrogenation of Pyrochlorin e.—Pyrochlorin e was reduced in glacial acetic acid in the usual way; 5.5 moles of hydrogen per mole of compound was absorbed when the reaction mixture had become colorless, which required about an hour and a half. On exposure to air without removal of the catalyst the solution became brown and on working up the product a porphyrin was obtained which was identical in spectrum in ether and acid solution with phylloporphyrin with the exception of a weak line at 652–645. In addition to this porphyrin a small amount of a chlorin was obtained which could be extracted with 7.5% hydrochloric acid; its spectrum was similar but not identical with Treibs and Wiedemann's phyllochlorin. This same phyllochlorin was obtained in better yields by the reduction using hydrogen iodide.

Reduction of Pyrochlorin e **with** Hydrogen Iodide.--Since the ester of pyrochlorin *e* was more readily available in a pure condition than the free acid, it was used for preparative purposes; in smaller runs with the free pyrochlorin *e* the results were identical. **A** 250-mg. sample of the pyrochlorin *e* ester was dissolved in 30 cc. of glacial acetic acid and 5 cc. of 45% hydriodic acid added; the color of the solution turned from a deep indigo-blue to a pure green. The flask containing the reaction mixture was then placed on the steam cone and heated for eight to ten minutes with frequent shaking. During this time the green color of the solution became lighter and the solution took on a yellowish-brown shade. The reaction mixture was immediately poured into 500–600 cc. of ether contained in a separatory funnel. On adding about 200 cc. of water and shaking vigorously the material went back in solution, and on standing for about an hour the ether solution became intensely green with a strong red fluorescence. Partially neutralizing the acid with ammonia immediately after transferring to ether seemed to accelerate the change to green. The extraction was then carried out in the usual manner after washing the ether solution several times with water to remove the acetic acid. Extraction with 1% hydrochloric acid removed phylloporphyrin along with a large proportion of another porphyrin with a line near 650. Extractions with 4 and 5% acid removed only small amounts of the green compound, which came out readily with 6 and 7% acid. These latter extracts contained the bulk of the coloring matter present and were colored pale blue. This main fraction, after transferring to ether, was esterified with diazomethane and concentrated for crystallization, a double volume of low-boiling petroleum ether being added. On standing overnight the material crystallized in round clusters of triangular plates with a deep blue luster and having a melting point of 148–150° on the block. In some preparations clusters of long hair-like needles appeared, but three recrystallizations from petroleum ether failed to raise the melting point above 150". The yield in this case was 140 mg. or 56% of the theoretical if the molecular weight of the material is considered to be the same as that of pyrochlorin *e* ester. **A** sample was tested for homogeneity by carefully fractionating and comparing the spectra of various fractions with the mother liquor. In every case the spectra compared were identical. In catalytic hydrogenation this chlorin required **3.3** moles of hydrogen per mole of compound for its conversion to the corresponding leuco-compound. On reoxidation phylloporphyrin was formed, as indicated by the comparison of its spectrum with known phylloporphyrin. There was, however, a weak line near 650 due to some impurity which is usually found in impure phylloporphyrin., In fact, this line appears in the reduction and reoxidation of pure phylloporphyrin.

The spectrum of the new phyllochlorin was as follows, in ether: I, 662.1---660.4—-632.1---620.4—615.1; **II,** 606.6---599.5—594.1---591.6—586.8; **III,** 552.4---549.7—544.3---540.5; IV, 525.3—519.5; V, 512.7---508—479.4; VI, ---455.8---; E. **A.,** 432.4. Order: I, V, **II,** IV, **III,** VI.

In **7%** Hydrochloric Acid.—I, 656.4---653.3—624.6---621.1; **II,** 606.6---588; **III,** 556---546.2; IV, 536---521.8; E. **A.,** 436.0. Order: I, 11, **IV,** 111.

Anal. (monomethyl ester). Calcd. for $C_{33}H_{40}O_2N_4$: C, 75.6; H, 7.6; N, 10.7; OCH_3, 5.9. Found: C, 75.44, 75.42; H, 7.75, 7.54; N, 11.06, 11.03; OCH_3, 6.77, 655.

The fraction of material containing phylloporphyrin from the hydrogen iodide reduction was esterified with diazomethane, after drying its ethereal solution, and refractionated with 0.5% hydrochloric acid. The ester thus obtained crystallized in the way characteristic of phylloporphyrin ester and melted at 230° on the block. A mixture with some known phylloporphyrin ester of melting point 235° melted at 230–233°. Comparison of its spectrum in ether and acid solution with known phylloporphyrin in the revision spectroscope showed the identity of the two spectra throughout.

Pyrochloroporphyrin.—The porphyrin mixture obtained in the pyrolysis of chlorin e as previously described amounts to about 150 mg. per gram of chlorin e. This material from 2 g. of chlorin e was dissolved in about three and one-half liters of ether with the aid of 10% acid. Fractionation of the resulting solution was begun with 0.3% acid. Each fraction of acid was washed twice with 300-cc. portions of ether before retransferring the colored matter to ether. With ten or fifteen extractions approximately one-third of the total material was removed, which appeared to be fairly pure phylloporphyrin as judged by a comparison of the spectrum with known phylloporphyrin. By continuing the extraction and gradually increasing the strength of acid to 0.4%, approximately one-quarter of the remaining coloring matter was removed. Comparison of its spectrum with the first fraction showed it to be a mixture. This second fraction was discarded. The wash ether was now replaced by fresh ether and the extractions continued using 0.5 and 0.6% acid. In this way approximately another third of the colored material was removed without finding any further change in spectrum. The spectrum of this material was easily distinguished from that of phylloporphyrin in the revision spectroscope. The mother liquor, though still quite colored, was discarded. The first and last fractions were then esterified and the resulting ether solutions of the esters subjected to fractionation. It was necessary in this case to use slightly more concentrated acid, since the esters were slightly higher in acid number than the free porphyrin acids. Thus the phylloporphyrin ester was extracted with 0.4 and 0.5% acid, while 0.6 or 0.8% acid was necessary for the convenient extraction of the pyrochloroporphyrin ester. This latter porphyrin solution was likewise washed first with 0.4 and 0.5% acid to remove further possible amounts of phylloporphyrin ester. In each case when about half of the coloring matter had been extracted, the mother liquors were discarded. The ethereal solutions of the extracted porphyrin esters were concentrated to a small volume for crystallization. The phylloporphyrin ester crystallized in the usual red prismatic needles, while the pyrochloroporphyrin ester appeared as long hair-like needles. Approximately 80 mg. of the former and 45 mg. of the latter were obtained. The yield is no criterion of the relative proportions of the two compounds present in the original mixture, since a large amount of the material was discarded. The mixture was judged to consist of approximately equal amounts of the two compounds. The material described in our first paper as "pyrochlorin e porphyrin" was undoubtedly more than 50% pyrochloroporphyrin, since this compound is much less soluble than phylloporphyrin, so that by recrystallization a considerable proportion of phylloporphyrin would be left in the mother liquor. The melting point of the phylloporphyrin ester was 235–236°, that of the pyrochloroporphyrin ester 226–237°. The former compound mixed with phylloporphyrin ester melted at 236–237°, while the latter also mixed with phylloporphyrin melted at 228–230°.

Spectrum of pyrochloroporphyrin ester in ether: I, 641.7—631.8; II, ---606.6--- III, 593.7---581.3—574.7---573.2; IV, 550.9---549.4—534.6---532.6; V, 522.8---521.1—487.8; E. A., 445.2. Order: V, IV, III, I, II.

The line previously recorded at 664–658 was obviously due to an impurity which has been removed in this fractionation. Spectrum in 1% acid: I, 609.0---599.0; II, 585.5---570.5—548.8---545.7; III, 526.2---514.2; E. A., 437.5. Order: 11, I, 111.

Anal. of methyl ester. Calcd. for $C_{33}H_{38}O_2N_4$: C, 75.85; H, 7.28; N, 10.73; OCH_3, 5.94. Found: C, 75.99; H, 7.45; N, 10.6; OCH_3, 6.3, 5.9.

Anal. of free acid. Calcd. for $C_{32}H_{36}O_2N_4$: C, 75.6; H, 7.09; N, 11.0. Found: C, 75.3, 75.0; H, 7.0, 7.2; N, 10.4, 10.2.

The spectrum of the phylloporphyrin ester fraction was identical in every detail with the spectrum of a known sample, compared line for line in the revision spectroscope.

A sample of the material designated as chloroporphyrin e_3 by Fischer and Moldenhauer[4] was prepared in the manner described by them. This sample was subjected to careful acid fractionation in the same way as the "pyrochlorin e porphyrin" mixture. The results were identical. The phylloporphyrin ester after its refractionation amounted to 45 mg. The pyrochloroporphyrin ester amounted to 43 mg. The crystal form in each case was the same as that of the corresponding fractions in the pyrolysis experiment: The spectra of the corresponding fractions in ether and acid were likewise identical in every detail as shown by direct comparison. The phylloporphyrin ester melted at 225–228°, and its mixture with a known sample melted at 230–234°. The melting point of the pyrochloroporphyrin ester was 226–230°, and when mixed with a sample of pyrochloroporphyrin ester prepared as above, gave no depression.

Reduction of Pyrochloroporphyrin.—A sample of pyrochloroporphyrin ester was dissolved in a few cc. of glacial acetic acid. A few drops of 45% hydriodic acid was added and the mixture was then heated on the steam cone for ten minutes. On transferring to ether and working up in the usual way, a major portion of the colored matter was extracted with 0.5% hydrochloric acid. This material was identical in spectrum both in acid and ether by direct comparison with known phylloporphyrin.

The spectrum as measured in ether was as follows: **I,** 633.0—628.5-–615.0 (hazy shadow); **II,** 606.6---601.8; **III,** **592.3---589.8—578.5-–573.1;** IV, 543.3---540.7—531.3---529.3; **V,** 519.6---516.8—486.2; **E.** A. 438.8. Order: V, **111, IV, I, 11.**

Another small sample of material was reduced catalytically to the leuco compound. The reduction may have been carried too far since the reoxidation took place very slowly. On retransferring to ether considerable scum was formed. However, a small amount of material could be extracted with 0.5% acid which checked in spectrum with known phylloporphyrin, though the ether solution was slightly brown and obviously impure.

Preparation of Dimethyl Phaeopurpurin 7 from Crude Phaeophytin.—A solution of 18 g. of crude phaeophytin (*a* and *b*) in 60 cc. of pyridine was added to 4 liters of ether and shaken for ten minutes with 400 cc. of a mixture of 25% potassium hydroxide in n-propyl alcohol. The solution turned deep green upon the addition of the alkali. Three liters of water was added to the saponification mixture and shaken; the alkaline layer was removed and the product transferred to 10 liters of ether by acidification. The ether solution, after washing with water and drying with sodium sulfate for ten minutes, was treated with an excess of diazomethane in ether solution. When a test showed that the product was alkali insoluble, the ether solution was extracted from eight to ten times with 1500-cc. portions of 11% acid. The acid solution used should be cold and all operations should be performed rapidly in order to prevent hydrolysis of the ester. Each acid extract was washed with 1500 cc. of ether in a 4-liter separatory funnel before transferring to ether. The material in the acid extracts was transferred to 8 liters of ether in all. This ether solution was washed with a 0.1 N solution of potassium hydroxide to remove some acidic material resulting from hydrolysis. Upon concentrating the ether solution, the dimethyl phaeopurpurin 7 crystallized in glistening hexagonal plates; the yield was 2–2.5 g.

Preparation of Phaeopurpurin 7.—A solution of 2.6 g. of dimethyl phaeopurpurin 7 in pyridine was added to 3 liters of ether and shaken for five minutes with 300 cc. of 25% n-propyl alcoholic potash. Water was added and the aqueous layer was acidified with shaking in the presence of 6 liters of fresh ether. The phaeopurpurin 7 was then extracted by 8% acid. The acid extracts were washed with ether through an intermediate separatory funnel and then the product was transferred to ether, 8 liters for all the extracts. The yield of phaeopurpurin 7 was 1.66 g.

A second procedure was adopted for preparing phaeopurpurin 7 which saved time but resulted in a slightly less pure product, The phase-test saponification of phaeophytin was carried out as described under the preparation of dimethyl phaeopurpurin 7. After methylation, instead of extracting the ester with 11% acid, the dry 10-liter ether solution (from 18 g. of phaeophytin) was shaken for five minutes with 500 cc. of 25% *n*-propyl alcoholic potash. Water was added and then the product was transferred back to the same ether solution by acidification. The resulting ether solution was then extracted with 8% acid until the color of extracts was a weak green. The acid extracts were washed with an equal volume of ether and transferred to 8 liters of fresh ether. The yield was 1.33 g. of phaeopurpurin 7.

Phaeopurpurin 18 and dimethyl phaeopurpurin 7 were relatively resistant to pyrolysis in diphenyl, as might be expected. Thus for the former it required five and one-half hours at 250° for the loss of 0.6 mole of carbon dioxide and for the latter four hours at the same temperature for 0.7 of a mole. The pyrolysis product was a complex mixture of porphyrins and chlorins which has not yet been separated into sufficient quantities of pure materials to warrant description.

Pyrolysis of Phaeopurpurin 7.—This substance lost one mole of carbon dioxide with comparative ease. A sample of 0.1630 g. was heated in diphenyl at the boiling point for ten minutes, the oil-bath was removed and the system swept with pure nitrogen for twenty minutes longer. The potash absorption bulb gained 11 mg., which corresponds to 96% of one mole of carbon dioxide lost by the sample. A sample of 0.1520 g. of phaeopurpurin 7, heated in diphenyl at 160–170° for forty-five minutes, lost 9 mg. of carbon dioxide, or 84% of one mole. An hour longer of heating at the same temperature did not change the weight of carbon dioxide. In addition to carbon dioxide, carbon monoxide was evolved. This was established by passing the gas through hemoglobin solution and noting the characteristic bands of CO-hemoglobin. The products resulting from the pyrolysis of phaeopurpurin 7 consisted of a mixture of porphyrins and one chlorin. The chlorin, which had an acid number of 11, and which we shall designate as monomethyl chlorin f was easily separated from the porphyrin mixture, since all the porphyrins were readily extracted by 5–9% acid. By laborious and careful fractionation, two porphyrins were isolated from the porphyrin mixture. One porphyrin had an acid number of 8, and the other 6. Besides the porphyrins 6 and 8 there are small amounts of some other porphyrins with lower acid numbers.

For preparative purposes, the pyrolysis was carried out on a larger scale. To a solution of 60 g. of boiling diphenyl was added 500 mg. of phaeopurpurin 7 and the solution heated at the boiling point for five minutes. After cooling, the diphenyl was poured into 500 cc. of ether and dilute alkali was added to extract the pyrolysis product. The alkaline solution was washed twice with fresh ether to remove all but traces of the diphenyl, and the pyrolysis product was then transferred to 2 liters of ether by acidification of the alkaline solution. The ether solution was extracted with 3 and 4% acids and then with 6–9% acids; the 9% extracts were washed with ether to remove traces of the chlorin. The chlorin was then extracted by means of 11–13% acids. The 6–9% acid porphyrin portion was separated by careful acid fractionation. The yields of the porphyrins were small. From 1 g. of phaeopurpurin 7 was obtained 70 mg. of the pyroporphyrin 8 and 30 mg. of the pyroporphyrin 6. The proportions of the two porphyrins and accompanying impurities may have varied with the method of pyrolysis and source of the phaeopurpurin 7, but this could not be checked exactly. Monomethyl chlorin f, which could he easily isolated and purified, was formed in 15–16% yields under all conditions; the yield from 1 g. of phaeopurpurin 7 was 150–165 mg.

Monomethyl Ester of Chlorin f.—This substance crystallizes from ether in eight-sided plates which approach an oval in contour. The acid number is 11, and the hydrochloric acid solution is pure blue. The ether solution is clear green without an olive tinge. The solubility in ether is about the same as that of chlorin e. The ether spectrum varies only slightly from that of chlorin e (1 mg. in 30 cc. ether): I, 684—647.5—637---631; II, 615—603; III, 563—553; IV, 531—524; V, 508—483.5; E. A. 433. Order: I, V, IV, II, 111.

The spectrum in 13% acid: I, 681—594; II, 577---568; III, 534---532—521--420; IV (very faint), 495---487; E. A. 447. Order: I. II, II, IV.

Anal. Calcd. for $C_{33}H_{40}O_4N_4$: C, 71.2; H, 7.2; N, 10.07; OCH_3, 5.6. Found: C, 71.4, 71.6; H, 6.6, 6.8; N, 10 0, 10.08; OCH_3, 6.1, 5.8.

Dimethyl Ester of Chlorin *f*.—This substance, prepared by the action of diazomethane on monomethyl chlorin *f*, or by the action of dimethyl sulfate on the alkaline solution, crystallizes from ether and methyl alcohol in rough aggregates of needles or sharp-pointed plates. The acid number lies between 13 and 14, and the acid solution is blue. The color and spectrum of the ether solution is the same as that of the monomethyl ester. The melting point is 182" (block). The hydrolysis of the ester (phase test conditions) yielded an alkali-soluble chlorin apparently identical with chlorin *f*; methylation with dimethyl sulfate regenerated the dimethyl ester.

Anal. Calcd. for $C_{34}H_{40}O_4N_4$: C, 71.8; H, 7.04; N, 9.86; OCH_3, 10.9. Found: C, 71.54, 72.0; H, 7.05, 6.9; N, 9.66, 9.88; OCH_3, 10.6.

The **Porphyrins** from Pyrolysis of Phaeopurpurin 7.—The porphyrin of acid number 8 is bluish-green in acid solution with a slight red fluorescence. It crystallizes from ether solution in stout diamond-shaped prisms. The spectrum in an ether-pyridine solution (1 mg. in 20 cc. of ether and 10 cc. of pyridine): I, 645---639; II, 595—580—571; III, 562—538; IV, 522—504; E. A., 444. Order: 111.11, IV, I.

The spectrum in 9% acid: I, 621–601; II, 585---574—543; III, 527---516; E. A., 444. Order: II, I, III.

Anal. Calcd. for $C_{33}H_{36}N_4O_4$: C, 71.7; H, 6.5; N, 10.15; OCH_3, 5.6. Found: C, 71.6, 71.8; H, 6.4, 6.5; N, 9.7; OCH_3, 6.3.

The porphyrin 6 crystallizes from ether in pointed plates with oval sides. The solution in acid is purplish-blue. The spectrum in ether solution: I, 675---660, faint shadow; II, 638—632.5; III, 590---576—571; IV, 552—539; V, 515—502---491; E. A , 436. Order: IV, V, III, II, I.

The spectrum in 6% hydrochloric acid: I, 608—600; II, 581---565—550---540; E. A., 435. Order: II, I.

The substance contains one methoxyl group; found, 6.52, 6.71% OCH_3.

Hot Saponification of Phaeopurpurin 7.—To a boiling solution of 30 g. of potassium hydroxide in 90 g. of n-propyl alcohol was added 400 mg. of phaeopurpurin 7 and the solution was refluxed for five minutes. The color of the solution was dark green with a deep red fluorescence. Water and ether were added and the mixture shaken. The aqueous alkaline layer was drawn off and the material transferred to 2 liters of fresh ether by acidification. The resulting ether solution was of a purplish-red color. The saponification product was a mixture of porphyrins and chlorin f. Acids of 4–8% extracted the porphyrins, leaving the ether colored green. The chlorin was extracted by 10–11% acids and transferred to fresh ether. Careful fractionation of the porphyrin extract with 5 and 6% acids removed the porphyrin of lower acid number. The material of higher acid number was in lesser amount and was not isolated. As the porphyrin of acid number 5 became more pure, more and more ether had to be used to keep it from crystallizing from solution. Finally, the pure porphyrin was contained in 4 liters of ether, from which was obtained 30 mg. of substance upon concentrating the ether solution. The yield of chlorin f was 111 mg. The same products were obtained when 35% potassium hydroxide in methyl alcohol was employed at the boiling point for thirty seconds.

Another saponification of phaeopurpurin 7 was carried out with the same quantity of material and procedure as described above. The saponification product, transferred to 3 liters of ether, was then methylated with diazomethane and the esters of the chlorin and porphyrin were fractionated from the ether solution. The porphyrin fraction was removed by 9% acid and the chlorin ester by 13–16% acid. The porphyrin ester corresponding to the insoluble porphyrin 5 was obtained by careful fractionation with 8% acid and washing the acid extracts with ether. Much material was lost as the ester during this acid fractionation—the acidic material was removed by washing the final ether solution with 0.1 *N* alkali. The yield of chlorin *f* ester was 146 mg.; of porphyrin 5 ester, 10 mg.

Potassium oxalate as a product of the reaction was demonstrated in another experiment; 400 mg. (0.6 of a millimole) of dimethyl phaeopurpurin 7 was hydrolyzed by boiling with 100 cc. of 25% methyl alcoholic potassium hydroxide for ten minutes. The reaction mixture was worked up in the usual way, the acidified aqueous layer being repeatedly extracted with ether and finally filtered through charcoal to remove all traces of the complex organic products. The aqueous solution was concentrated, made faintly alkaline with ammonia and calcium chloride added to the hot solution. The precipitate was washed with dilute acetic acid and collected on a microfilter; it weighed 39 mg. On treatment with dilute hydrochloric acid 30 mg. (0.23 millimole) of calcium oxalate dissolved. The calcium oxalate was reprecipitated from the hydrochloric acid solution, filtered off, dissolved in sulfuric acid and titrated with standard permanganate. The total oxalate thus determined was 20 mg. of calcium oxalate (0.16 millimole). Considering the losses encountered in the manipulations, the quantity of oxalate found corresponds to the yield of chlorin f and the accompanying porphyrin (about 40%). In a "control experiment" chlorin e was substituted for phaeopurpurin 7 and the same procedure employed; no calcium oxalate was obtained.

Chlorin *f*.—This substance is very insoluble in ether, from which it crystallizes in microscopic prismatic needles barely visible at a magnification of 60 diameters. The acid number is 10 and the color in acid solution is deep blue. The solution in ether is green without the olive tint characteristic of chlorin e. The spectrum in ether: I, 685—645---631; II, 617—603; III, 561---554; IV, 531—524; V, 510—481; E. A., 436. Order: I, V, IV, II, III. The spectrum in 12% hydrochloric acid: I, 680—629---611—597; II, 577---568; III, 535---521; E. A. 439. Order: I, III, II.

Anal. Calcd. for $C_{32}H_{38}O_4N_4$: C, 70.9; H, 7.05; N, 10.34. Found: C, 71.7, 71.4; H, 6.3, 6.6; N, 10.0, 10.3; OCH_3, 0.

A Porphyrin from the Saponification of Phaeopurpurin 7.—This porphyrin was obtained in very small quantities and is characterized by its insolubility in ether and the solubility in dilute alkali. It dissolves readily in 0.1 N potassium hydroxide with a pink solution. The acid number lies between 5 and 6; the color of the acid solution is light blue with a purplish-red fluorescence. It contains no methoxyl group. It appears to be the dibasic acid corresponding to porphyrin 6 from the pyrolysis experiments. The spectrum in ether solution: I, 637---632; II, 593---578—573; III, 557---553—542---537; IV, 518---511—503---492; E. A., 436. Order: III, IV, II, I. Spectrum in 0.1 N potassium hydroxide: I, 664—650; II, 574---556; III, 549---537; IV, 513—496; E. A., 436. Order: I, IV, III, II. Spectrum in 6% acid: I, 616.5—598; II, 585---573—541; 111,524---511 (very faint); E. A., 440. Order: 11, I, III.

Action of Hydriodic Acid on Dimethyl Ester Chlorin f.—A solution of 20 mg.

of chlorin f dimethyl ester in 30 cc. of glacial acetic acid was heated on a steam cone for ten minutes with 2 cc. of 45% hydriodic acid. The brownish-red reaction mixture was poured into ether and the acetic acid was washed out with water and ammonia. Finally, the ether solution was extracted with dilute alkali, which removed most of the material, and the product was transferred to fresh ether by acidification. Fractionation with 6% acid removed a porphyrin, leaving a green solution. The porphyrin on further purification proved to be identical with rhodoporphyrin in acid number, color and spectrum in acid and ether solution. The green solution was washed with 9% acid and then the chlorin removed with 12% acid. The chlorin had a spectrum somewhat similar to those of the "synthetic chlorins" reported by Fischer: I, 680—638 (two maxima); II, 627.5—621; III, 608—593; IV, 563---545; V, 531---525—510.5; VI, 508—478.5; E. A. 438. Order: I, VI, III, V, II, IV.

Pyrolysis of Chlorin f.—A 0.1029-g. sample of chlorin f was heated in diphenyl at 240–260° for twenty minutes; 1.7 mg. of carbon dioxide was lost. After heating for two and one-half hours longer at the boiling point of diphenyl, the loss of carbon dioxide in all was 4.6 mg. This corresponds to over 50% of one mole of carbon dioxide. The result may not be accurate due to the small weight of sample. The pyrolysis product was a mixture of porphyrins from which was obtained by fractionation with 1.5–2% acid, a considerable amount of pyrroporphyrin. The remainder of the material was of higher acid number. The pyrroporphyrin was identical in acid number, color and spectra in acid and ether solutions with a known sample of pyrroporphyrin. A mixed melting point of the esters showed no depression.

Alkali Decomposition of Monomethyl Chlorin f.—A mixture of 65 mg. of monomethyl chlorin *f*, 6 cc. of 25% methyl alcoholic potassium hydroxide, 3 cc. of pyridine and 50 mg. of magnesium oxide was heated at 150–156° for five hours in a silver-lined autoclave.[5] The decomposition product was shaken with 20% hydrochloric acid and transferred to a liter of ether. The red ether solution, without purification, checked in color and spectrum with an authentic sample of rhodoporphyrin. Fractionation showed the presence of only one substance which were removed by 4–5% acid. The color and spectrum in ether and acid solution were identical with those of rhodoporphyrin. The fractionated material was converted to the methyl ester by the use of diazomethane. The ester crystallized from ether in rectangular plates, characteristic of rhodoporphyrin dimethyl ester. The melting point was 255°, and a mixed melting point with a known sample of dimethyl rhodoporphyrin showed no depression.

Alkali Decomposition of the Porphyrins from the Pyrolysis of Phaeopurpurin 7.—A 20-mg. sample of porphyrin 6 and a 10-mg. sample of porphyrin 8 were heated in separate silver crucibles with proportionate amounts of alkali, pyridine and magnesium oxide according to the procedure of Treibs and Wiedemann, to 150–160° for five hours. The phyllins were decomposed with 20% acid and the products transferred to ether. In each case rhodoporphyrin was the sole product. The material was identicai in color and spectrum in ether and acid solution, and in acid number, with authentic rhodoporphyrin.

Saponification of Allomerized Chlorophyll.—Crude chlorophyll[6] (from spinach) was separated into the *a* and b components by Willstatter's procedure. The pure chlorophyll *a* gave the "phase test" and on rapid saponification yielded chlorin *e* with only a trace of material with higher acid number. Samples of this pure chlorophyll *a* were allomerized by standing in absolute alcohol solution for twenty-four to forty-eight hours; the allomerization was demonstrated by the failure of the resultant material to give the phase color. A solution of 150 mg. of allomerized chlorophyll in alcohol was diluted

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[5] Treibs and Wiedemann, *Ann.*, 471, 174 (1929).

[6] We are indebted to Dr. H. A. Spoehr for supplying the crude chlorophyll.

with water and ether and the material thus transferred to dry ether in the usual way. The ether solution was evaporated to dryness in a silver container and the residue treated with 15 cc. of boiling alcoholic potassium hydroxide, **(35%)** and the boiling continued for thirty seconds. On diluting with water and acidification with concentrated hydrochloric acid, the color change showed the removal of magnesium. On working up the product in the usual way, including the treatment of the unstable chlorins with diazomethane, dimethyl phaeopurpurin 7 was the main product. It was identified by its color, acid number, spectrum in ether, in 12% hydrochloric acid and, after hydrolysis, in 0.1 *N* alkali (the spectra were compared with a known sample in a revision spectroscope); as a by-product a porphyrin ester with acid number about 8 was obtained. In another experiment allomerized phaeophytin *a* was prepared by treating allomerized chlorophyll *a* with concentrated hydrochloric acid. The rapid hot saponification of the allomerized phaeophytin *a*, followed by the diazomethane treatment in the usual way, yielded dimethylphaeopurpurin 7 and only a trace of higher chlorins; the porphyrin appeared to be absent.

Summary

1. It has been shown that the saponification of allomerized chlorophyll *a* yields phaeopurpurin 7, a characteristic product of the phase test; allomerization and the phase test appear to be equivalent processes.

2. Phaeopurpurin 7 (a monomethyl ester) on pyrolysis loses carbon dioxide and carbon monoxide, forming the monomethyl ester of a simple chlorin which appears to be a hydrogenated rhodoporphyrin. The corresponding dibasic acid is formed by the action of hot alcoholic potassium hydroxide on phaeopurpurin 7, oxalic acid being split off. These facts show that phaeopurpurin 7 is an α-keto acid.

3. Pyrochlorin e is a simple chlorin of the unallomerized series; it still contains the carbon atom which is eliminated as carbon monoxide in the allomerized compound. It appears to be isomeric with phylloporphyrin. All these facts point to an oxidation–reduction process as being involved in the phase test and allomerization.

CAMBRIDGE, MASSACHUSETTS

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

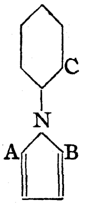
THE STEREOCHEMISTRY OF N-PHENYLPYRROLES. THE PREPARATION AND RESOLUTION OF N-2-CARBOXYPHENYL-2,5-DIMETHYL-3-CARBOXYPYRROLE. XIII[1]

BY L. H. BOCK[2] AND ROGER ADAMS

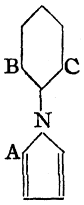
RECEIVED DECEMBER 15, 1930 PUBLISHED JANUARY 12, 1931

The search for the presence of stereoisomerism in certain substituted molecules containing rings of an aromatic or semi-aromatic type is a natural development from the study of diphenyl compounds. Such a field, the study of which is being undertaken in this Laboratory, includes compounds in the series of the phenylpyridines, dipyridyls, phenylpyrroles, phenylpyrazoles, etc. The difficulty of synthesis, however, is a severe hindrance to the rapid development of the study of these types. Only recently has the first dicyclic compound other than a diphenyl been found in which this type of isomerism exists. The compound was a phenylquinone.[1a] In all of the researches connected with the various substances just mentioned the attachment of one ring to the other has been attempted always through carbon linkages.

A preliminary study has now been made to determine whether certain properly substituted dicyclic compounds with carbon–nitrogen linkages between the rings might not show similar isomerism. A class of such compounds which has interesting possibilities is the N-phenylpyrroles represented by the general structures (I), (II) and (III). This communication describes a compound which belongs to Type I. It is N-2-carboxyphenyl-2,5-dimethyl-3-carboxypyrrole (IV), prepared by condensing anthranilic acid with 3-carbethoxy-2,5-hexadione (prepared from chloroacetone and acetoacetic ester) and then saponifying. Resolution was effected by means of the brucine salt. The same remarkable difference in solubility between the two diastereoisomericsalts exists as in the salts from previously resolved diphenyl compounds.



I



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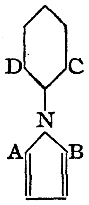
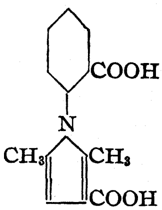


III



IV

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[1] For the preceding papers in this series see (a) Shildneck and Adams, THIS JOURNAL, 53, 343 (1931); (b) Stoughton and Adams, *ibid.*, 52, 5263 (1930).

[2] This communication is a portion of a thesis submitted by L. H. Bock in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

The active forms do not racemize upon boiling for eight hours in ethyl alcohol. They are, however, essentially completely racemized upon boiling for twenty-four hours in 0.1 *N* sodium hydroxide solution.

If the usual explanation of the phenomenon in the diphenyl series is applied here, it may be said that there is restricted rotation between the benzene ring and the pyrrole ring due to the interference of the ortho substituted groups. Whether the same conditions for the appearance of the phenomenon hold as in the diphenyl series is to be determined, However, the possibility must not be overlooked that in this molecule the optical activity may be dependent, not upon the restricted rotation but upon the character of the nitrogen atom or it may be dependent on a combination of the two. Experiments which are now under way and which will be reported soon should indicate with considerable certainty whether this latter explanation is likely, and at that time a detailed discussion of the theoretical possibilities will be given.

Based on the results just described, optical activity may also be expected in properly substituted N-phenyltetrazoles, N-phenylpyrazoles, N-phenylpyrrodiazoles, etc., as well as in the ortho substituted dicyclic compounds with the two nitrogens attached to each other as in N,N-dipyrroles, N,N-dipyrazoles, N,N-ditetrazoles and N,N-dipyrrodiazoles, etc. Representatives of these classes are being prepared.

Experimental

3-Carbethoxy-2,5-hexadione.—This compound was previously prepared by Weltner[3] from monochloroacetone and acetoacetic ester. In a 1-liter, three-necked flask equipped with a mercury-sealed stirrer, reflux condenser and dropping funnel were placed 260 g. of acetoacetic ester and 25 g. of sodium. The mixture was stirred at room temperature until all of the sodium had dissolved. This required about twenty-four hours. Then 250 cc. of dry ether was added and 99 g. of monochloroacetone was slowly added. Stirring was continued for eighteen hours. The reaction mixture was filtered, washed with water and extracted with ether. The product distilled at 95–105° (3 mm.). The yield was 96 g. (48% of the theoretical amount).

N-2-Carboxyphenyl-2,5-dimethyl-3-carboxypyrrole.—A solution of 18.6 g. of 3-carbethoxy-2,5-hexadione and 13.7 g. of anthranilic acid in 100 cc. of absolute ethyl alcohol was refluxed for one hour. The reaction mixture was then refluxed for fifteen minutes with alcoholic sodium hydroxide, filtered, cooled and acidified with dilute hydrochloric acid. Eight grams of crude product precipitated. It was purified by crystallization from one liter of ethyl acetate containing a little alcohol; m. p. 224.5–225.5°. It is soluble in alcohol, ether and acetic acid but only slightly soluble in ethyl acetate and chloroform.

Anal. Calcd. neut. equiv.: 129.6. Found: 128.6. Calcd. for $C_{14}H_{13}O_4N$: C, 04.84; H, 5.0. Found: C, 65.33; H, 5.1.

Resolution of **N-2-Carboxyphenyl-2,5-dimethyl-3-carboxypyrrole.**—A solution of 15.5 g. of brucine in 400 cc. of dry ethyl acetate was added hot to a suspension of 10 g. of N-2-carboxyphenyl-2,5-dimethyl-3-carboxypyrrole in 400 cc. of hot ethyl acetate. A

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[3] Weltner, *Ber.*, 17, 67 (1884).

clear solution resulted from which the brucine salt precipitated when the side of the beaker was rubbed with a stirring rod. The mixture was cooled and filtered, yielding *12.8* g. of salt which gave $[\alpha]_D$ *—37".* On concentrating the filtrate, *10* g. of salt of $[\alpha]_D$ +12° was obtained. The first fraction was recrystallized from *200* cc. of absolute alcohol to constant rotation. The more soluble fraction was recrystallized from ethyl acetate.

I-Salt.—0.1137 g. made up to *15* cc. with chloroform at 20° gave α_D —0.68°; *l = 2;* $[\alpha]^{20}_D$ —44.9°; m. p. 231–232° (dec.).

Anal. Calcd. for $C_{37}H_{39}O_8N_3$ (monobrucine salt): C, *67.96;* H, *6.0.* Found: C, *67.74;* H, *6.1.*

d-**Salt.**—0.1551 g. made up to *15* cc. with chloroform at 20° gave α_D *\$0.28";* *l = 2;* $[\alpha]^{20}_D$ +13.5°; m. p. 175–180° (dec.).

Anal. Calcd. for $C_{37}H_{39}O_8N_3$: C, *67.96;* H, *6.0.* Found: C, *67.71;* H, *6.1.*

d- and l-N-**2-Carboxyphenyl-2,5-dimethyl-3-carboxypyrroles.**—The salts were decomposed by shaking in a separatory funnel with dilute hydrochloric acid and ether. The acid went into the ether layer and was obtained by evaporating to dryness. The acids were crystallized from ethyl acetate to constant rotation.

I-Acid.—0.1349 g. made up to *15* cc. with absolute alcohol at 20° gave α_D *—0.49';* *l = 2;* $[\alpha]^{20}_D$ –27.2°; m. p. 203–204°.

d-Acid. *—0.1753* g. made up to 15 cc. with absolute alcohol at 20° gave α_D + *0.63;* *l = 2;* $[\alpha]^{20}_D$ + 27.0°; m. p. *202–204".*

Racemization Experiments.—About *0.3* g. of *l*-compound in *50* cc. of absolute alcohol was boiled for eight hours. No change in initial rotation took place. In boiling glacial acetic acid, the rotation dropped to nearly zero in one hour but there was obviously decomposition occurring which probably accounted for this. Only a gram could be recovered from the heated solution.

A solution of 0.2107 g. of I-acid in *25* cc. of *0.1 N* sodium hydroxide gave an initial rotation of α_D —0.39"*([or]* $^{20}_{D}$ *—23.1).* After eighteen hours' standing at room temperature, no change occurred. Upon boiling for twenty-four hours, the rotations were as follows: *1* hr., a_D *—0.39";* *4* hrs., *or,* *—0.31°;* *8* hrs., α_D —0.26°; *24* hrs., α_D —0.03°. Upon acidification racemic acid was obtained, m. p. *224–225".*

Summary

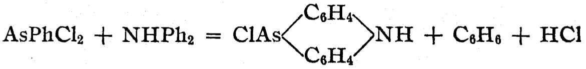
The preparation and resolution of N-2-carboxyphenyl-2,5-dimethyl-3-carboxypyrrole has been described.

URBANA, ILLINOIS

NOTES

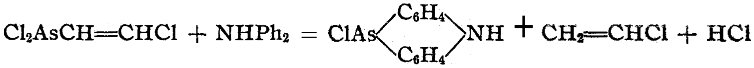
The Reaction between Dichloro-arsines and Secondary Aromatic Amines.—Lewis and Stiegler [THIS JOURNAL, 52,4164 (1930)] appear to have overlooked work already published on this subject.

Burton and Gibson [J. *Chem. Soc.,* 464 (1926)] having shown that the reaction between phenyldichloro-arsine and diphenylamine did not yield 10-phenyl-5,10-dihydrophenarsazine but 10-chloro-5,10-dihydrophenarsazine according to the equation



$$AsPhCl_2 + NHPh_2 = ClAs\left<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right>NH + C_6H_6 + HCl$$

were led to compare the analogous reaction using β-chlorovinyldichloroarsine as described by Lewis and Stiegler [This Journal, **47**, 2546 (1925)]. They found (*loc. cit.*, p. 466) that not only is 10-chloro-5,10-dihydrophenarsazine and not "6-chlorovinylphenarsazine" formed by the action of β-chlorovinyldichloro-arsine on diphenylamine, but, by proving the production of vinyl chloride in the reaction, showed that the course of the latter may be expressed



$$Cl_2AsCH{=}CHCl + NHPh_2 = ClAs\begin{matrix}C_6H_4\\ \\C_6H_4\end{matrix}NH + CH_2{=}CHCl + HCl$$

Burton and Gibson also proved that the reaction between phenyldichloroarsine and other substituted diphenylamines and of β-chlorovinyldichloroarsine and phenyl-a-naphthylamine proceeds analogously. These results have since then been fully verified by Seide and Gorski [*Ber.*, 62, 2186 (1929)]. Scherlin and Epstein [*Ber.*, **61**, 1823 (1928)] have also shown that the reaction between β-chloro-ethyldichloro-arsine and diphenylamine yields 10-chloro-5,10-dihydrophenarsizine, the reaction being quite similar.

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C. S. Gibson

Received November 3, 1930
Published January 12, 1931

Phenylmagnesium Fluoride.—The relative reactivities of RX compounds with magnesium in ether is in the order RI > RBr > RCl > RF. Actually, only one RMgF compound (n-amylmagnesium fluoride) has been prepared, and this synthesis was effected by unusually extensive refluxing with a large quantity of iodine.

In connection with studies concerned with improved catalysts for the formation of organomagnesium halides, it was observed that none of the highly active catalysts induced a reaction between fluorobenzene and magnesium in ether. There has been described recently a satisfactory method for the preparation of phenylmagnesium chloride in the absence of a solvent, and this method is distinctly superior to the very slow formation of this compound when ether is used with varying quantities of iodine and with the magnesium–copper alloy.[1] In this study involving no solvent and a sealed tube it was shown that when fluorobenzene was heated with magnesium at 300° for about 200 hours, a small quantity of diphenyl formed. The formation of diphenyl is almost certain evidence for the intermediate formation of phenylmagnesium fluoride,[2] and the statement was made that this Grignard reagent would probably be prepared by heating at a lower (as yet undetermined) temperature for a longer time.

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[1] Gilman and St. John, *Rec. trau. chim.*, 49, 717–723 (1930).

[2] Gilman and Brown, This Journal, 52, 5045 (1930).

It now appears, in strict accordance with our knowledge of the very deliberate rate of reaction of chlorobenzene and magnesium in ether,[1] that even the most refractory RX compound will probably react with magnesium in ether if sufficient time be permitted for such a reaction. This finds support in some studies made in sealed, small test-tubes wherein it has been shown that fluorobenzene undergoes reaction with the activated magnesium-copper alloy in ether after being allowed to stand at room temperatures for eighteen months, and that phenylmagnesium fluoride is formed. Individual tubes opened at intervals of one month showed no positive color test at the end of six months. Reaction, therefore, had set in some time between six and eighteen months. Quite probably a compound like *p*-difluorobenzene will form *p*-fluorophenylmagnesium fluoride more readily, because *p*-dichlorobenzene reacts more readily than chlorobenzene.

It is altogether reasonable to expect that a distinctly shorter time will be required for the formation of phenylmagnesium fluoride when the proper temperature range in sealed-tube experiments is determined or when superior catalysts are discovered. At present, however, if one desires a pure RMgX compound from a highly inert RX compound, it is merely necessary to enclose the reactants in a container to exclude the atmosphere and moisture and wait for the reaction to run its course. The compensations for such devastating delays are that the RMgX compound will almost certainly be of a high order of purity and will be formed in a high yield because side reactions are drastically reduced with the use of relatively inert RX compounds. The difficulties in most cases are more apparent than real because of the ready accessibility of the related RBr and RI compounds. In our case we needed phenylmagnesium fluoride in studies on the relative reactivities of some organometallic compounds.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
IOWA STATE COLLEGE
AMES, IOWA

HENRY GILMAN
LLOYD L. HECK

RECEIVED NOVEMBER 3, 1930
PUBLISHED JANUARY 12, 1931

A New Compound of Benzaldehyde and Anthrahydroquinone.—During an investigation on the autoxidgtion of anthrahydroquinone in benzaldehyde solution,[1] it was found that such a solution (oxygen being excluded), when containing a trace of hydrochloric acid, gave on standing in the dark at room temperature for twelve to seventy-two hours a new compound in good yield. The presence of benzoic acid appeared to favor larger yields. No reaction occurred: (1) in the absence of hydrochloric acid; (2) with anthrone substituted for anthrahydroquinone; or (3) between anthrahydroquinone and either benzoic acid or benzoin in acetone solutions.

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[1] Backstrom and Beatty, to be published.

Since free anthrahydroquinone is awkward to handle on account of its oxidizability, a more convenient. preparation of the compound is as follows. Take 250 cc. of commercial benzaldehyde, 10 g. of anthraquinone, 10 g. of benzoic acid, 1 cc. of hydrochloric acid and 20 cc. of ethyl alcohol (to favor the photo-reduction of the anthraquinone):[2] seal the container to exclude oxygen and expose the mixture to sunlight or other illumination until the anthraquinone has dissolved. Steam distil the solution to remove aldehyde, etc., then treat the remaining tar with enough alcohol and ether to dissolve the resinous matter, leaving a dry, crystalline residue, Dissolve this in hot alcohol and add two volumes of filtered sodium hydrosulfite solution (100 g. of hydrosulfite and 100 g. of sodium hydroxide per liter of water) and two volumes of water: the anthraquinone remains in solution, and the compound may be filtered off and recrystallized from alcohol or acetone. The yield is only about 10% of the anthraquinone taken.

The compound is slightly soluble in ether, acetone and 95% alcohol (0.6 g. per 100 cc. at the boiling point), and readily soluble in hydrocarbons; the solutions are not fluorescent. It dissolves in concentrated sulfuric acid with a red color turning brown. Acetone and alcohol solutions give identical crystals—large, colorless, hexagonal tablets—melting at 211–212° (corr.) with decomposition and sublimation of anthraquinone.

Aqueous alkali is without effect on the compound; alcoholic alkali causes a very slow hydrolysis; with alcoholic hydrochloric acid the action is faster (20 mg. per hour per 25 cc.). The products of hydrolysis are benzaldehyde, qualitatively detected by its odor, and anthrahydroquinone, distinguished by its characteristic fluorescence which disappears on shaking with air.

ANALYSES

Calculated values are for $C_{14}H_8(OH)_2 + 2C_6H_5CHO - H_2O = C_{28}H_{20}O_3$

	C, %	H, %	Mol. wt.[a]	Anthraquinone, %[b]	Benzaldehyde, %[c]
Found	82.91	5.00	416 ± 20	51.8 ± 1.5	52.7 ± 1.0
	83.03	4.97	405	50.2	
				50.2	
Calcd.	82.94	4.99	404.3	51.49	52.48

[a] By the method of Menzies and Wright, THIS JOURNAL, 43, 2309 (1921). [b] By spectrophotometric analysis (Ref. 1) of a solution of the hydrolyzed material. [c] By precipitation, from a similar solution, of the *p*-nitro-phenylhydrazone (the melting points of the precipitated and synthetic hydrazones were identical, 187.5–188° (uncorr.)).

The properties and analyses of this substance indicate a structure of the quinone and of the acetal type, containing no free hydroxyl or acyl groups, and probably derived by condensation of two molecules of benz-

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[2] Compare, Meyer and Eckert, *Monatsh.*, 39,249 (1918).

aldehyde with one of oxanthrone (the tautomeric form of anthrahydroquinone).

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HAROLD A. BEATTY

RECEIVED NOVEMBER 5, 1930
PUBLISHED JANUARY 12, 1931

Note on the Interaction of Tertiary Butyl Chloride and Naphthalene.—Wegscheider[1] had studied the reaction between isobutyl chloride and naphthalene in the presence of anhydrous aluminum chloride and had obtained isobutylnaphthalene boiling at 280°. The so-called isobutylnaphthalene was probably a-tertiary butylnaphthalene, b. p. 278–287°, which was later prepared from a-naphthylmagnesium bromide and *tert.*-butyl bromide by Späth.[2]

Besides the liquid butylnaphthalene, Wegscheider had also obtained a small amount of two solid substances, one crystallizing in fine, white needles of m. p. 80° and the other forming white leaflets or prisms of m. p. 146–147°. Wegscheider thought that probably the lower-melting compound was α,β-dinaphthyl and the substance of m. p. 146–147° was α,α-dinaphthyl (m. p. 154°), being somewhat impure and therefore of depressed melting point.

The writer tried to prepare *tert.*-butylnaphthalene from one mole of *tert.*-butyl chloride and one mole of naphthalene using a small amount (about 1% of the combined weight) of aluminum chloride as catalyst and finally heating the mixture just above its melting point until no hydrogen chloride came off. A liquid mono-*tert.*-butylnaphthalene of b. p. 280° never was formed; on distilling the reaction product, about half a mole of naphthalene was recovered and a fraction boiling over 300° was obtained. On changing the proportions of the starting materials to two moles of *tert.*-butyl chloride and one mole of naphthalene, practically all of the naphthalene was converted into two isomeric di-*tert.*-butylnaphthalenes which could be separated by fractional crystallization from methanol or ethanol. The one as the main product is quite soluble in these alcohols and forms fine, white needles of a salol-like odor. The substance melts at 82–83' and boils at 319'.

Anal. Subs., 0.1200, 0.1285: CO_2, 0.3960, 0.4230; H_2O, 0.1075, 0.1139. Calcd. for $C_{18}H_{24}$: C, 89.93; H, 10.07. Found: C, 90.03, 89.91; H, 10.03, 9.92.

The other di-*tert.*-butylnaphthalene, melting at 145–146° and boiling at 320°, crystallizes in white prisms and is not easily soluble in alcohol.

Anal. Subs., 0.1271, 0.1205: CO_2, 0.4185, 0.3963; H_2O, 0.1147, 0.1086. Calcd. for $C_{18}H_{24}$: C, 89.93; H, 10.07. Found: C, 89.93, 89.72; H, 10.10, 10.09.

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[1] Wegscheider, *Monatsh.*, 5, 238 (1884).

[2] Späth, *ibid.*, 34, 2013 (1913).

An attempt was made to establish the position of the *tert.*-butyl groups in the naphthalene ring by means of boiling the di-*tert.*-butylnaphthalenes with dilute nitric acid, but no oxidation to the naphthalene-dicarbonic acids took place.

Very probably Wegscheider had already obtained these two isomeric di-*tert.*-butylnaphthalenes but his belief that his compounds of m. p. 80° and 146–147° were *α,β*-dinaphthyl and *α,α*-dinaphthyl was erroneous.

CONTRIBUTION FROM THE
RESEARCH LABORATORY OR
DEHLS AND STEIN
NEWARK, N. J.
WILLIAM GUMP

RECEIVED NOVEMBER 25, 1930
PUBLISHED JANUARY 12, 1931

COMMUNICATIONS TO THE EDITOR

PHOTOCHEMICAL REACTIONS OF GASEOUS METHYL IODIDE

Sir:

In a recent communication to Nature, Iredale[1] has discussed the action of light upon gaseous methyl iodide. From a study of the short wave limit of the absorption spectrum, he calculates the energy of the C–H bond to be 65 Cal. and suggests, with Herzberg and Scheibe,[2] that the initial process is the dissociation of methyl idodide into CH_3 and I, since the absorption is continuous. Studies of the photochemical decomposition and oxidation of gaseous methyl iodide in progress in this Laboratory for some time past lend additional support to the idea that CH_3 and I are the initial products. The reaction behaves as though the process were actually that of the oxidation of free methyl groups. Formaldehyde, paraformaldehyde and methylal seem to be the products, while the iodine originally present in the methyl iodide can in all cases be recovered as free iodine.

A possible mechanism for the process is

$$\begin{aligned} CH_3I &\longrightarrow CH_3 + I \\ CH_3 + O_2 &\longrightarrow CH_2O + OH \\ CH_3I + OH &\longrightarrow CH_3OH + I \\ 2CH_3OH + CH_2O &\longrightarrow (CH_3O)_2CH_2 + H_2O \end{aligned}$$

Kinetic measurements are being made to determine the actual mechanism.

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JOHN R. BATES
ROBERT SPENCE

RECEIVED DECEMBER 1, 1930
PUBLISHED JANUARY 12, 1931

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[1] Iredale, Nature, 604, Oct. (1930).

[2] Herzberg and Scheibe, *Trans. Faraday Soc.*, *25*, 716 (1929).

THE THERMAL CHLORINATION OF METHANE BY A FLOW METHOD

Sir:

We have recently been investigating the thermal (non-catalytic) chlorination of methane by a flow method. The following conclusions as to the kinetics of the reaction may be of interest.

The reaction takes place readily in pyrex glass reaction tubes above about 200° at 1 atm. total pressure. The rate is unaffected if the reaction tube is packed with broken glass, or if the internal surface of the tube is coated with potassium chloride. The reaction is, therefore, homogeneous. The effects of changes in concentration of reactants indicate that it is also bimolecular.

At the lower temperatures (225–300°) the reaction is inhibited by oxygen. Thus at 225° and five minutes' heating, 30% of the chlorine reacts when the reaction mixture consists of 60% methane and 40% chlorine at 1 atm. With 5% of oxygen present there is no measurable reaction. At 300° the suppression by oxygen is still considerable, but at 375°, at which temperature the rate of the unsuppressed reaction is very high, 5% of oxygen has no measurable effect. This effect of oxygen points to a chain mechanism. This is borne out by a discrepancy between the observed reaction rate at any temperature and that calculated by the collision theory of bimolecular gas reactions. About 1000 more molecules react than the theory predicts. A recent study of the photochemical chlorination of methane by Coehn and Cordes [Z. *physik.* Chem., Abt B, 9, 1 (1930)] has demonstrated that a chain mechanism applies here also, chains being some 10^4 molecules in length at the maximum.

This work is being extended and will be later reported in full.

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PRINCETON, NEW JERSEY

ROBERT N. PEASE[1]
GEORGE F. WALZ[2]

RECEIVED DECEMBER 10, 1930
PUBLISHED JANUARY 12, 1931

ADSORPTION AND PROMOTER ACTION IN CATALYSIS

Sir:

The results of Elissafoff's experiments [*Z. Electrochem.*, 21, 352 (1915)] have been quoted by Hugh S. Taylor in his "Treatise upon Physical Chemistry" and also by Rudel and Haring [*Ind.* Eng. Chem., 22, 1234–1237 (1930)] as an example of adsorption in catalysis. The first investigator found that copper sulfate in the presence of glass wool decomposed hydrogen peroxide more rapidly than either substance alone, and that the effect was greater than the sum of the individual effects. Since separate experiments showed that a glass powder, of the same composition as the

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[1] Research Associate, American Petroleum Institute.

[2] Research Assistant, American Petroleum Institute.

glass wool, removed copper from solution, Elissafoff concluded that the copper was adsorbed at the interface and that the increased concentration of copper was responsible for the increase of rate. This conclusion was justified by close parallelism between the increased rate of reaction when the copper concentration was increased tenfold, and the increased amount of copper removed from a solution of similarly increased copper concentration.

At the time my attention was called to this article, I conducted a few brief tests with results incompatible with those of Elissafoff. The experiments could not be amplified for lack of time, and therefore it seems best to indicate them briefly now. Hydrogen peroxide solutions were decomposed in quartz vessels by freshly prepared copper sulfate solutions containing one millimole per liter of copper sulfate. It was found that the velocity constant was nearly first order and not easily reproduced in the presumably neutral solutions employed. It is felt that the data from one series of experiments may be compared among themselves, however. It was also found that the addition of glass wool to a solution containing hydrogen peroxide and copper sulfate did increase the rate of decomposition hut to a less extent than Elissafoff observed. The reaction velocities for the promoted reaction increased appreciably with time, which points to a dependence of rate upon an adsorbed catalyst. However, it was found that a filtered extract of the glass wool increased the rate quite as much as the solid material. Also it was found that increasing the amount of glass wool ten-fold increased the rate of reaction very little. From these observations it was concluded that the glass wool no doubt removed copper from solution as Elissafoff says, but not as copper sulfate. The copper probably formed a basic salt upon the surface of the glass wool, and then solid copper peroxide, a reaction which is favored by the alkali from the glass. The reaction in the absence of glass wool can be and probably is homogeneous; thus it seems probable that the mechanism of the reaction is different under "promotion" conditions than otherwise, and that this reaction is not an example of the effect of adsorption upon catalytic reaction rates.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
A. C. ROBERTSON

RECEIVED DECEMBER 5, 1930
PUBLISHED JANUARY 12, 1931

THE OXIDATION OF CARBON MONOXIDE BY DISSOCIATED WATER VAPOR

Sir:

In a recent publication Harteck and Kopsch[1] have shown that atomic oxygen, from a discharge tube, has very little effect on carbon monoxide;

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[1] Harteck and Kopsch, *Z. Elektrochem.*, **36,** 714 (1930).

only 5% reacted. At the suggestion of Professor Hugh S. Taylor we have carried out experiments on the action of dissociated water vapor on carbon monoxide. It seems entirely probable that in the water vapor discharge tube[2] we have a source of hydroxyl, also the reaction[3] $OH + CO = CO_2 + H$ is 24,000 cal. exothermic. That we do get oxidation is shown by the results given in Table I.

TABLE I

RESULTS OF EXPERIMENTS

Water through tube, mole	CO, mole	CO converted to CO_2, %
0.039	0.005	21.60
.059	.005	26.30

We have also passed a constant quantity of oxygen through the tube and then varied the water vapor concentration. It is to be pointed out that the exit of the tube did not become very warm, which means that the water vapor was not decreased to such an extent that recombination of the atomic oxygen took place on the walls. Also, there was no back diffusion to the discharge tube in any of the experiments. The results are given in Table II.

TABLE II

EXPERIMENTAL DATA

Water through tube, mole	Oxygen, mole	CO, mole	CO converted to CO_2, %
0.003	0.028	0.005	5.90
.012	.028	.005	24.30
.059	.028	.005	37.10

Since Copeland[4] has found that water vapor is essential for the production of atomic oxygen, we can attribute the oxidation in Harteck and Kopsch's experiment to the presence of a small quantity of water.

Further details will be published shortly.

DEPARTMENT OF CHEMISTRY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

G. I. LAVIN
W. F. JACKSON

RECEIVED DECEMBER 13, 1930
PUBLISHED JANUARY 12, 1931

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[2] Lavin and Stewart, Proc. *Nat. Acad. Sci.*, 15, 829 (1929); Taylor and Lavin, THIS JOURNAL, 52, 1910 (1930).

[3] Bonhoeffer and Haber, *Z. physik. Chem.*, A137, 263 (1928).

[4] Copeland, Phys. Rev., 36, 1221 (1930).

NEW BOOKS

Handbuch der anorganischen Chemie. (Handbook of Inorganic Chemistry.) By Dr. R. ABEGG, Dr. FR. AUERBACH and Dr. I. KOPPEL. Die Elemente der achten Gruppe des periodischen Systems. Eisen und seine Verbindungen. (The Elements of the Eighth Group of the Periodic System. Iron and its Compounds.) Second part, B, Lieferung 1. S. Hirzel Königstrasse 2, Leipzig, Germany 1930. xvi + 462 pp. 139 figs. 17 × 24 cm. Price, unbound, M. 45.

In a preface to this instalment Dr. Koppel, the sole surviving editor of this Treatise, states that it had been the intention to issue the volume on Iron as a complete whole, but that delays in its preparation had made it desirable to issue it in two parts, A and B. A is to deal with the iron atom, iron metal, alloys, the compounds of iron with the metalloids other than the halogens, its passivity, corrosion, technology and analysis. B is to deal with the compounds of iron.

The present volume (B 1) constituting the first part of B, discusses the compounds of di- and trivalent iron other than the complex cyanides, the compounds of hexavalent iron, the carbonyls and nitrosyls of iron and a number of substances which according to the opinion of various investigators are derived from mono-, tetra- and pentavalent iron.

This volume maintains the valuable features characteristic of the earlier volumes of this Treatise, namely, a connected, clear and critical presentation of the subject matter from a broad theoretical standpoint.

ARTHUR B. LAMB

Elementary Practical Physical Chemistry. BY FRANK SHERWOOD TAYLOR, M.A., B.Sc., Chemistry Master at Gresham's School, Holt. Oxford University Press, American Branch, New York, 1928. xi + 130 pp. 51 figs. 12.5 × 18.5 cm. Price, $1.25.

The scope of the book is indicated in the preface, in which the author says: "This book has been written for the use of the advanced classes of schools and the first-year classes of the universities. It assumes that no apparatus is available other than that found in every school laboratory, and also that the student's time is strictly limited."

The contents of the book may be summarized as follows: Part I includes the usual procedures for the determination of molecular weights, osmotic pressures and dissociation. Part II deals with ionization (the author calls it "the ionic hypothesis"), particularly with such subjects as electrolysis, solubility products, indicators, complex ions, and the e. m. f. series. In Part III, besides the usual experiments on reaction velocities, several exercises are included dealing with the effects of temperature, concentration, light and catalysis on the speed of reactions. Part IV includes three simple experiments on the distribution of a solute between two solvents. Part V deals with heterogeneous equilibria, in which certain applications of the phase rule are introduced. Part VI is an introductory treatment of colloids, consisting of easy preparation methods.

Many of the experiments are qualitative rather than quantitative, and in all cases the theroetical basis of the experiment is briefly outlined. Many teachers might find the book useful as a source of lecture table and extra laboratory experiments.

J. H. REEDY

Volumetric Glassware. By VERNEY STOTT, B.A., F.Inst.P., Senior Assistant, National Physical Laboratory; Formerly Scholar of Peterhouse, Cambridge, England. H. F. and G. Witherby, 326 High Holborn, W. C., London, England, 1928. 232 pp. 40 figs. 14 X 22 cm. Price, 20 s. net.

The units of volume, their origin and history, are discussed in Chapter I. Tables are given showing the corrections to be added to apparent weight of water at observed temperature to give volume in ml. at standard temperature. The details of construction of measuring flasks and graduated cylinders, a device for determining the internal diameter of the necks of flasks at the graduation mark, general instructions for graduating and testing, are ably discussed. The tolerances and specifications of the National Physical Laboratory are stated in detail and a comparison is made with the tolerances and specifications of the United States Bureau of Standards. The author points out that satisfactory graduations for burets and graduated cylinders require that every numbered graduated line (every tenth line) extend completely around the cylinder or buret and the remainder at least half-way around. The effect of drainage based on delivery time of pipets and burets has been carefully studied and precautions outlined so that best results may be obtained.

The machines used for placing the graduation marks on volumetric apparatus are described, especial attention being given to those used for placing the graduations on burets and graduated cylinders in conformity with the specifications of the National Physical Laboratory and the U. S. Bureau of Standards.

A series of Calibration Tables useful in calibrating and testing volumetric apparatus completes the volume.

The book gives an excellent treatise on volumetric glassware and the information contained would be very useful to manufacturers, users and those engaged in calibrating and testing such apparatus.

E. L. PEPPER

An Introduction to Organic Chemistry. By ERIC JOHN HOLMYARD, M.A., M.Sc., D.Litt., F.I.C., Head of the Science Department, Clifton College. Longmans, Green and Co., 55 Fifth Avenue, New York, 1930. xi + 282 pages. Illustrated. 12.5 × 19 cm. Price, $1.75.

This excellent elementary textbook is based upon the author's "Outlines of Organic Chemistry" and "is intended for complete beginners—boys and girls who have just passed the School Certificate examination and are now about to enter upon the wider field of study that lies invitingly before them." It contains clear directions for many experiments and interesting discussions of the simpler portions of organic chemistry theory, but it does not cover as wide a field as is usually covered by the most elementary courses which are given in this country. It makes no mention, for example, of the Grignard reaction, of tautomerism or of the relation between color and chemical constitution.

We cannot refrain from quoting the first paragraph of Chapter One. "Those about to begin the study of organic chemistry stand at the threshold of a new world, a world of entrancing beauty and surpassing interest. With sufficient resemblance to inorganic chemistry to render its features not completely unfamiliar, it nevertheless has characteristics of its own that excite the admiration of the simple tourist, captivate the permanent settler and stimulate the explorer to penetrate its utmost recesses. There cannot be many, and there should not be any, dull moments in the study of organic chemistry. And for the novice there is the reassuring fact that organic theory is easy, logical and almost invariably obeyed, the rare exceptions serving mainly to impart a slightly piquant effect to the whole, like a *retroussé* nose upon a profile otherwise severely Grecian."

Following shortly after this is a section entitled "A Day's Experience," in which the many contacts of a London business man with the products and materials of organic chemistry are enumerated. After he has reached his office, "feeling a little stuffy in the nose, he uses his ***artificial silk*** handkerchief (made of cellulose dyed with an organic dye), upon which he has taken the precaution to sprinkle a few drops of ***eucalyptus oil,***" etc. And in the evening he "finally arrives home to a savoury organic dinner, washed down with organic beer and followed by an organic cigar." The book has a distinctly British and a distinctly pleasing atmosphere.

Holmyard's book is too elementary for the short courses in organic chemistry which are offered at American colleges. But we are not acquainted with a better book for the uses of the exceptionally bright high-school student who wishes for an acquaintance with organic chemistry beyond the scope of the regular high-school inorganic chemistry course.

TENNEY L. DAVIS

Gesammelte Abhandlungen zur Kenntnis der Kohle. (Collected Contributions to the Knowledge of Coal.) Vol. 9. By Professor Dr. FRANZ FISCHER, Director of the Kaiser-Wilhelm-Institut für Kohlenforschung. Verlag von Gebrüder Borntraeger, W 35 Schöneberger Ufer 12a, Berlin, Germany, 1930. viii + 759 pp. Illustrated. 16.5 X 25.5 cm. Price, bound, M. 70.

This volume is a collection of papers describing work done at the Kaiser Wilhelm Institute for Research on Coal chiefly during the years 1928 and 1929. The papers are for the most part reprints of papers already published elsewhere, principally in *Brennstoff-Chemie.* There are included, however, some sixteen papers not previously published, as well as an Appendix containing a history of the Institute, a description of the new Lecture Hall erected in 1929 and an account of its dedicatory exercises.

The researches described here are in part continuations of the earlier researches of the Institute relative to the origin and constitution of coal and the coal-formers, and extend them, for instance, on the biological side. Other researches are concerned with the chemical and technological problems of fuels, particularly the production of coke. Finally, there are many researches dealing with the purification of gases, catalysis and the thermal and electrical treatment of gases, all of which point to the increasing importance of synthetic fuel.

The articles are arranged under the following heads:

I. Bacteriological Researches
II. Lignin, Humic Acid and Related Fields
III. Origin and Constitution of Coal
IV. Montanic Acid
V. Chemical and Technological Researches on Coal
VI. Researches on Gases. (a) Gas purification. (b) Benzine synthesis. *(c)* Catalytic, thermal and electrical treatment of gases
VII. Carbides
VIII. Miscellaneous Articles and other Publications. Appendix: History of the Institute.

The unpublished articles are particularly concerned with the bacteriological study of coal and with the synthesis of benzine.

This volume is at once a most convenient collection of related articles and a striking demonstration of the success of the Kaiser Wilhelm Institute under the leadership of Dr. Franz Fischer.

ARTHUR B. LAMB

Die **Globuline.** (The Globulins.) By Dr. MONA SPIEGEL-ADOLP, Assistant at the Institute of Medical Colloid Chemistry of the University of Vienna. Vol. IV, "Handbuch der Kolloidwissenschaft." Verlag von Theodor Steinkopff, Residenzstrasse **32,** Dresden-Blasewitz, Germany, **1930.** xv + **452** pp. **68** figs. **15.5** X **23.5 cm**. Price, unbound, RM. **33;** bound, RM. **35.**

The distinctive chemical properties of the globulins, and their very widespread occurrence in living tissues, mark them out as among the most important of proteins. With acids and bases they are as reactive as the albumins, while their great change in solubility with changing salt concentration sets them apart from other proteins. The study of this property offers a wide and important field of physico-chemical investigation, and will undoubtedly throw light on the biological function of the globulins.

Dr. Mona Spiegel-Adolf's book is the first comprehensive monograph devoted specifically to this class of proteins. It opens with a long chapter on the occurrence of globulins in nature, the methods used in separating them from other substances, and their chemical composition and structure. Two chapters follow on the reactions of globulins with acids and bases, and the associated physico-chemical phenomena, which are treated in great detail. All those chapters deal with aspects of protein behavior in which the globulins do not fundamentally differ from the albumins, while Chapter IV deals with the distinctive behavior of globulins in neutral salts. Chapter V discusses their interaction with colloids and salts of heavy metals; and the final chapter treats of the globulins in biology and medicine, especially in their relation to immunity.

The author has gathered together a great amount of material from the most diverse sources, and has presented it very fully, with a wealth of tables and diagrams. The presentation of the work discussed is so full and so impartial that this monograph should be of great value as a work of reference.

The discussion is devoted almost entirely to the serum globulins and cdestin; the globulins of other plant and animal tissues are scarcely more than mentioned. In our present state of ignorance concerning these substances, this is probably inevitable; but this gap indicates clearly the need for further study in this important field. Even the serum globulins remain very ill-characterized, as compared with such proteins as egg albumin or hemoglobin. Dr. Spiegel-Adolf's presentation of what has already been done makes clear the need for further exact studies in many directions: both in the preparation of pure globulin solutions, and in the analytical and physico-chemical study of their properties.

The most characteristic property of globulins, their solution and precipitation by neutral salts, might well have been treated more fully. The work of Osborne and Harris on the solubility of edestin, for instance, remains a model of investigation in this field, and deserves presentation at greater length. Moreover, the original valence rule applied by Mellanby to the solvent action of neutral salts on serum globulin is clearly a special form of the ionic strength principle later formulated by G. N. Lewis, and theoretically elucidated by Debye and Huckel. The theories of Debye and Hückel have indeed already been successfully applied to some protein systems. They deserve some discussion in such a book as this, for they promise to throw light on aspects of protein behavior which have hitherto remained perplexing and obscure.

JOHN T. EDSALL

BOOKS RECEIVED

JOHN S. ANDERSON, Editor. "Photo-electric Cells and Their Applications." A Discussion at a Joint Meeting of the Physical and Optical Societies, June 4 and **5, 1930.** Published by the Physical and Optical Societies, **1** Lowther Gardens, Exhibition Road. South Kensington, London S. W. **7,** England. 236 pp. 12 s./6 d.

T. V. BARKER. "The Study of Crystals." Thomas Murby and Co., London. **137** pp. **8 s./6 d.**

T. V. BARKER. "Systematic Crystallography." Thomas Murby and Co., London. 115 pp. **7** s./6 d.

BARNARD S. BRONSON. "Nutrition and Food Chemistry." John Wiley and Sons, Inc., New York. 467 pp. **$3.75.**

RUSSELL H. CHITTENDEN. "The Development of Physiological Chemistry in the United States." The Chemical Catalog Co., New York. **427** pp. **$6.00.**

C. DRUCKER, Editor. "Ostwald-Luther. Hand- und Hilfsbuch zur Ausfiihrung physikochemische Messungen." Fifth, revised edition. Akademische Verlagsgesellschaft m. b. H., Leipzig, **Germany.**

W. T. HALL. "Textbook of Quantitative Analysis." John Wiley and Sons, Inc., New York. **279** pp. ***$2.50.***

NICOLAAS HENDRIK VAN HARPEN. "The Electrometric Determination of the Hydrogen Ion Concentration in the Latex of *Hevea Brasiliensis* and its Applicability to Technical Problems." Varekamp and Co., Medan, Holland. **459** pp.

VICTOR HERBERT NOLL. "Laboratory Instruction in the Field of Inorganic Chemistry." The University of Minnesota Press, Minneapolis, Minnesota. **164** pp. **$2.00.**

Wo. OSTWALD, Editor. "Organische Chemie und Kolloidchemie." Verlag von Theodor Steinkopff, Dresden-Blasewitz, Germany. 124 pp.

DAVID REICHINSTEIN. "Grenzflächenvorgänge in der unbelebten und belebten Natur." Verlag Johan Ambrosius Barth, Leipzig, Germany. **434** pp.

FRITZ SCHMIDT. "Die Zustandsgrössen des Sauerstoffs bei tiefen Temperaturen mit Diagrammen." VDI-Verlag G. m. b. H., Berlin. 20 pp. RM. 4.

HERMANN ULICH. "Chemische Thermodynamik. Einführung in die Lehre von den chemischen Affinitaten und Gleichgewichten." Verlag von Theodor Steinkopff, Dresden-Blasewitz, Germany. **353** pp. RM. **18.50,** unbound; RM. **20,** bound.

HENRY S. WASHINGTON. "The Chemical Analysis of Rocks." Fourth edition. John Wiley and Sons, Inc., New York. 296 pp. ***$4.00.***

RENÉ WURMSER. "Oxydations et Réductions." Les Presses Universitaires de France, **49** Boulevard Saint-Michel, Paris. **381** pp. ***95*** francs.

F. ***H.*** ZSCHACKE. "Glas, seine Herstellung und Verwendung." Verlag von Theodor Steinkopff, Dresden-Blasewitz. Germany. **208** pp. RM. **12,** unbound; RM. **13.50.** bound.

The Journal of the
American Chemical Society

VOL. 53 FEBRUARY, 1931 NO. 2

[Contribution from the Missouri School of Mines and Metallurgy]

THE SOLUBILITIES OF ALKALI CHLORIDES AND SULFATES IN ANHYDROUS ALCOHOLS

By E. R. Kikn and H. L. Dunlap

Received June 2, 1930 Published February 9, 1931

A search of the literature for information on the solubilities of inorganic salts in various anhydrous alcohols will show that comparatively little work has been recorded. Most of the data have been obtained for salts in aqueous alcohols[1] and practically all these data concern only methyl and ethyl alcohols. The solubilities of salts in these alcohols show a wide variation with different investigators. These discrepancies in results may be attributed to varying amounts of water in the alcohols, or the methods for determination may have permitted moisture to reach the solutions.

Most of the data are for one temperature only. No reference was found on the solubilities of sodium and potassium chlorides and sulfates in the lower alcohols over a wider range of temperature. Thus it was thought that such a study might show some relationship between the solubility of a salt in the various alcohols and their increasing molecular weight.

Preparation and Purification of Materials.—The salts used were Baker's c. p. salts. These salts were further purified by two recrystallizations from distilled water. After the final recrystallization, the salts were washed, pulverized and dried in an electric oven at a temperature of 150° until they gave no further loss in weight. They were then transferred to tightly fitting ground-glass stoppered bottles and kept until needed.

The alcohols were first carefully fractionated[2] using the fraction that boiled within 0.5° of the correct boiling point as accepted in the "International Critical Tables." After this fractionation, the alcohols were placed over freshly calcined lime and allowed to stand with frequent shaking, for several days, depending upon the alcohol. Methyl and ethyl alcohols were allowed to stand for a longer time. Then, after refluxing for twelve hours, the alcohols were decanted from the lime and again fractionated, the fraction boiling nearest the accepted boiling point being

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[1] (a) Landolt-Bornstein, "Physikalish-Chemische Tabellen," pp. 730–737; (b) C. A. Lobry de Bruyn, *Z. physik. Chem.*, 10, 783 (1892).

[2] Brunel, Crenshaw and Tobin, This Journal, 43, 561–577 (1921).

collected. This fraction was then further dehydrated by the use of aluminum amalgam.

The aluminum amalgam was prepared by refluxing mercury with sandpapered aluminum chips for twelve hours. About 200 g. of this amalgam was used per liter of alcohol.

After standing over the amalgam for several days, the alcohols were carefully decanted to avoid the possibility of the formation of aluminum alcoholates[3] and again fractionated, retaining that fraction which checked the accepted boiling point within 0.2°, pressure and stem corrections being made. To test this method for dehydrating the alcohols, solubility tests on ethyl alcohol were made using potassium chloride as the solute. After its first dehydration with aluminum amalgam, a solubility determination was made and then the alcohol was again treated with aluminum amalgam and a solubility determination repeated at the same temperature. These two determinations checked very closely. In the final fractionation, the alcohols were distilled into double capped ground-glass stoppered bottles. At all times during distillations they were protected from moist air by means of calcium chloride tubes.

Apparatus.—The thermostat was similar to that developed by Goodhue and Dunlap.[4] The thermostat was electrically heated and the temperature controlled to a tenth of a degree. The method of agitation was the same as that used in the above reference.

The method for obtaining samples was similar to that devised by Weber and Dunlap,[5] but a few modifications were made to adapt it to this work It was found more practical to use a 500-cc. Kjeldahl flask provided with a well-rolled cork stopper which had been extracted previously with alcohol. A strip of thin rubber, provided with two small holes for the condenser and the sampling tube, was fastened over the cork and top of the flask to prevent moisture from coming in contact with the cork. The lower end of the sampling tube was fitted with a shortened Soxhlet thimble for filtering out the suspended salts. By forcing dry air into the flask through the driers at the top of the condenser, a sample of any amount could be taken. To prevent the thimble from removing some of the dissolved salt by adsorption, the solution was first forced back and forth through the thimble while the outlet was protected by a drying tube. The thimble was raised out of the solution during the agitation.

Procedure.—The alcohols were carefully transferred to the flasks and an excess of dry pulverized salt was added. The condenser with the filtering apparatus was attached and placed in the thermostat, with the flask submerged. The time of agitation for saturation was determined by

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[3] Berger, *Compt.* rend., 157, 717–718 (1906).

[4] Goodhue and Dunlap, THIS JOURNAL, 50, 1916–1922 (1928).

[5] Weber and Dunlap, *Ind. Eng. Chem.*, 19, 481 (1927).

experimentation. It was found that an hour and a half was sufficient in most cases, but more time was always allowed. After equilibrium had been reached, 25 cc. was removed; after one hour and a half, a check sample was also removed. These were collected in tightly fitting ground-glass stoppered bottles, cooled to room temperature in a desiccator and weighed.

With the chlorides, the contents of the weighing bottles were transferred to casseroles, diluted with water to about 50 cc. and then titrated with standard silver nitrate solution, using potassium chromate as an indicator. This method was checked by running blank determinations with C. P. sodium chloride having present 25 cc. of the alcohol. The two butyl alcohols, however, are immiscible with water so they were first evaporated to dryness, taken up in water, and then titrated as above.

The solutions containing the sulfates were transferred to weighed casseroles and carefully evaporated to dryness, and then reweighed. Checks were made on all determinations and only those which gave reasonably close checks were averaged for the final data. The average deviation of these check determinations was about 0.5% in the methanol, 2% in the ethanol and propanol, and 4% in the isopropanol, butanol and isobutanol solutions. These data calculated to moles of solute per mole of solvent are recorded in Table I.

TABLE I

MOLES OF SALT PER MOLE OF ALCOHOL

Temp., °C.	NaCl	KCl	Na_2SO_4
	Methanol		
20	0.00778	0.00833	0.00555
30	,00758	.00729	.00544
35	.00744	,00691	.....
40	,00734	.00642	,00523
45	,00720	.00528	.....
50	,00711	,00415	.00415
	Ethanol		
20	0.001147	0.001270	0.00143
30	.001197	.001378	,00154
35	.001242	,001443	.....
40	,001258	.001454	,00156
45	,001293	,001277	.....
50	.001142	.000845	.00114
	Propanol		
20	0.0000446	0.0000700	Insoluble
30	.0000434	,0000796	Insoluble
35	,0000421	.0000793	Insoluble
40	0000417	.0000773	Insoluble
45	.0000384	.0000683	Insoluble
50	,0000337	.0000473	Insoluble

Temp., °C.	NaCl	KCl	Na_2SO_4
	Isopropanol		
20	0.00096	0.001235	0.000886
30	.00100	.001300	.000939
35	.00108	.001340	.....
40	.00102	.001390	,000928
45	.00102	.001295	.....
50	,00093	.001060	.000739
	Butanol		
20	0.0000695	0.0000822	Insoluble
30	.0000710	.0000852	Insoluble
40	,0000762	,0000904	Insoluble
50	.0000774	,0000925	Insoluble
	Isobutanol		
20	0.0000280	0.0000326	Insoluble
30	,0000292	.0000356	Insoluble
40	.0000341	.0000400	Insoluble
50	.0000356	,0000407	Insoluble

Summary

Anhydrous potassium sulfate was found to be insoluble in all the alcohols used, and sodium sulfate is soluble in only three of the alcohols. The solubility of sodium sulfate in methyl alcohol increases with a rise in temperature. In ethyl and isopropyl alcohols, the solubility of sodium sulfate reaches a maximum and then decreases. The solubilities of the sulfates in alcohols follow the general trend of their solubilities in water, that is, the sodium being more soluble than the potassium sulfate.

The chlorides of both sodium and potassium in methyl alcohol show a slight decrease in solubility with temperature. In ethyl, n-propyl and isopropyl alcohols both salts pass through a maximum solubility and then decrease, the potassium decreasing more rapidly than the sodium chloride. In the butyl alcohols there is a slight increase in solubility with rise of temperature for both salts.

The solubility of all the salts decreases as the molecular weight of the alcohol increases.

ROLLA, MISSOURI

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE COMPRESSIBILITY ISOTHERMS OF METHANE AT PRESSURES TO 1000 ATMOSPHERES AND AT TEMPERATURES FROM –70 TO 200°

BY HAMLINE M. KVALNES AND V. L. GADDY

RECEIVED JUNE 6, 1930 PUBLISHED FEBRUARY 9, 1931

The formation of methane as a side reaction in high pressure syntheses involving hydrogen and carbon monoxide and its use as a reactant have emphasized the need of compressibility data for the gas over a wide pressure and temperature range. Previously existing data on the compressibility of methane are for the temperature range 0 to 200° at pressures to 300 atmospheres. Amagat[1] determined the compressibility of methane for temperatures between 14.7 and 100.1° at pressures from 40 to 300 atmospheres. The absolute volumes are not given but only PV relative to the volume of a certain manometric tube. Burrell and Robertson[2] measured an isotherm at 15° to a pressure of forty atmospheres. Keyes, Smith and Joubert[3] determined five isotherms for the temperatures 0, 50, 100, 150 and 200° at pressures to about 300 atmospheres. Later Keyes and Burks[4] improved the apparatus used by Keyes, Smith and Joubert, and redetermined the data for the same temperatures and approxi-

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[1] Amagat, *Ann. Chim. Phys.*, 22, 367 (1881).

[2] Burrell and Robertson, Bureau of Mines Technical Paper No. 158 (1917).

[3] Keyes, Smith and Joubert, *J. Math. Phys. Mass. Inst. Tech.*, 1, 191 (1922).

[4] Keyes and Burks, THIS JOURNAL, 49, 1403 (1927).

mately the same pressure range. In the present work the data are extended to cover the temperature range −70 to 200° at pressures to 1000 atmospheres.

Method, Apparatus and Calibrations.—The method and apparatus used in the present experiments are, for the most part, the same as those already fully described in papers from this Laboratory dealing with the compressibility of carbon monoxide, hydrogen, nitrogen and mixtures of the latter two.[5] The only modification made in the equipment consisted in simplifying the former purification train to contain only two low temperature traps, one packed in ice and the other in solid carbon dioxide.

The 20-cc. bronze pipet used at the lower pressures was calibrated with hydrogen before and after the zero degree work on methane. All other pipet calibrations were made with methane at 0°.

All temperatures were controlled by hand in a manner similar to that formerly described[6] for control of temperatures below 0°. The thermocouple was the same as that used in the aforementioned work and has since then been compared with another copper–constantan thermocouple calibrated by the Bureau of Standards at temperatures of −25.92, −50.42 and —70.50'. The latter calibration was made against a platinum resistance thermometer, "standardized in the manner provided in the definition of the International Temperature Scale." It was considered accurate to about one microvolt, which is equivalent to about 0.03° in the temperature range —25 to −70°. The comparison indicated that the low temperatures were —24.99 ± 0.03°, —49.93 ± 0.03° and —69.90 ± 0.03°, for the listed temperatures of —25, —50 and −70°.

Calculations.—To determine the compressibility factor at a given pressure and temperature by the method employed in this work, it is necessary to measure the quantity of gas contained in a pipet of known volume at the given pressure and temperature. To do this the gas is allowed to expand into a larger volume where it is measured at 25° and at a pressure ranging from 480 to 1000 mm., according to the quantity of gas obtained. It is desired, however, to know the volume of gas at 760 mm. and 0°. The temperature change is calculated by using the temperature coefficient of expansion α for the gas. For gases such as hydrogen and nitrogen it is sufficiently accurate to correct the gas to 760 mm. by the ideal gas law. Methane, however, differs significantly from the ideal gas even at atmospheric pressure. The value for PV at 760 mm. and 0° is given in the "I. C. T."[6] as 0.9976. P V was assumed equal to 1 at zero pressure and the value for any other pressure was taken

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[5] **Bartlett, This Journal, 49, 68 (1927); 49, 687 (1927); 49, 1955 (1927); Bartlett, Cupples and Tremearne,** *ibid.*, **50, 1275 (1928). Bartlett, Hetherington, Kvalnes and Tremearne,** *ibid.*, **52, 1363 (1930); 52, 1374 (1930).**

[6] **"International Critical Tables," Vol. III, p. 3.**

from a straight line through the two points. Using the above correction for change of compressibility with pressure, samples measured at the two extremes of the pressure range checked to within 0.05%.

Gas.—The 500 cubic feet of methane gas required for this investigation were made available to the Fixed Nitrogen Research Laboratory through the courtesy of the du Pont Ammonia Corporation. It was prepared from a mixture of hydrogen and methane by condensation at the temperature of liquid air and subsequent fractional distillation to remove traces of dissolved hydrogen. The previous history of the gas precluded the presence of nitrogen. Ordinary methods of analysis failed to show any other impurities. Other tests[7] indicated a purity of 99.88 ± 0.02%.

Experimental Results

The experimental results are given in Table I. Each PV value with the exception of those given for zero and one atmosphere pressure is the average of two or more separate determinations. At all temperatures determinations were made at pressure intervals sufficiently small accurately to define the shape of the isotherms. At the lowest temperatures this necessitated obtaining a few data at pressure intervals of five atmospheres.

The PV value at zero pressure and 0° was taken as the reciprocal of the aforementioned "I. C. T." value of 0.9976, which agreed to better than 0.1% with the value obtained by extrapolation of the PV–P curve through the points at 1, 30 and 40 atmospheres. The remaining values at zero pressure were calculated, using the ideal gas temperature factor, while those at one atmosphere were taken from a curve drawn through the zero, 20, 30 and 40 atmosphere points.

Figure 1 is a plot of the isotherms obtained by dividing each PV value by the value at zero pressure for that temperature. The curves thus all have the same origin, that is, $PV = 1$, at zero pressure. They are drawn through every experimentally determined point, and in all cases give smooth curves.

Discussion

The data obtained by Keyes and Burks[4] on the compressibility of methane have been incorporated in Table I. Their results are given in specific volumes so that it was necessary to calculate the corresponding PV values and plot them for the pressures given in order to obtain the values of the table at the even pressures. No extrapolations beyond the range of pressures examined by Keyes and Burks were made. The error in plotting was less than 0.05%.

The range of temperature and pressure in this work duplicates the

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[7] Dr. Rossini of the Bureau of Standards used some of this gas in an investigation to be published in the *Bureau of Standards Journal of Research.* He found by analysis 0.12% of CO, and combustion ratios of carbon to hydrogen checked this value.

TABLE I

THE COMPRESSIBILITY FACTORS, PV, FOR METHANE

Atm.	−70°	−50°	−25°	0"	+25°	+50°	+100°	+150°	+200°
0	0.7455	0.8189	0.9106	1.0024	1.0942	1.1859	1.3695	1.5530	1.7365
1	.7410	.8150	,9075	1.0000	1.0922	1.1845	1.3686	1.5525	1.7363
20	.6473	.7402	....	....	1.0549	....	....	....	....
30	.5910	.6991	.8183	0.9303	....	1.1412	1.3411	1.5370	1.7311
	....	....	....	,9292"	....	....	....	....	....
40	.5244	.6547	.7873	,9065	1.0198	1.1284	....	....	....
	....	....	....	,9057"	....	1.1267'	....	....	....
50	.4425	.6069	....	.8833	....	....	1.3268	1.5319	1.7309
	....	....	....	.8827[a]	....	....	1.3269"'	....	....
60	.3366	,5551	.7243	,8611	0.9871	1.1020	....	1.5305	1.7306
	....	....	....	,8603"	....	1.1014[a]	1.3205[a]	1.5280[a]	1.7301[a]
65	.2912	....	....	....	....	....	....	....	....
70	.2633	.5059	....	....	....	....	....	....	....
80	.2556	.4604	.6651	.8199	.9569	1.0806	....	....	....
	....	....	....	,8185"	....	1.0792'	1.2018"	1.5248"	1.7322"
90	....	.4266	....	....	....	....	....	....	....
100	.2808	.4088	.6167	.7853	.9319	1.0636	....	....	....
	....	....	....	.7836[a]	....	1.0612[a]	1.3018"	1.5237"	1.7357[a]
120	.3175	.5095	.5877	,7604	.9126	1.0498	....	....	....
	....	....	....	....	....	1.0476"	1.2965[a]	1.5241[a]	1.7414[a]
140	.3543	,4304	.5801	,7457	,9003	1.0408	....	....	....
	....	....	....	....	....	1,0390"	1.2939"	1.5272"	1.7485"
160	.3915	,4601	.5891	,7425	.8949	1.0367	....	....	....
180	.4288	,4924	.6079	.7482	.8970	1.0373	1.2995	....	....
	....	....	....	....	....	....	1.3000"	1.5398"	1.7668"
200	,4656	.5269	.6319	.7631	.9048	1.0437	1.3076	1.5504	1.7760
	....	....	....	....	....	....	....	1.5497"	1.7788"
250	.5567	,6142	.7066	.8184	.9469	1.0776	1.3364	....	1.8107
	....	....	....	....	....	....	....	....	1.8151"
300	,6458	.7025	.7879	.8886	1.0062	1.1286	1.3785	1.6234	1.8534
400	.8185	,8750	.9561	1.0468	1.1499	1.2608	1.4929	1.7268	1.9586
500	,9867	1.0433	1.1221	1.2086	1.3064	1.4106	1.6277	1.8542	2.0813
600	1.1487	1.2071	1.2862	1.3709	1.4659	1.5653	1.7729	1.9935	2.2131
700	1.3066	1.3661	1.4466	....	....	....	....	....	....
800	1.4631	1.5246	1.6046	1.6894	1.7801	1.8781	1.0744	2.2828	2.4949
900	1.6154	1.6782	1.7607	....	....	....	....	....	....
1000'	1.7656	1.8287	1.9110	2.0000	2.0892	2.1845	2.3757	2.5797	2.7851

[a] Keyes and Burks, THIS JOURNAL, **49,** 1403 (1927).

pressure range of Keyes and Burks[4] at 0 and 50°, while at the three higher temperatures they duplicate only the extremes of the pressure ranges. Throughout the entire pressure range for 0 and 50°, the present results are higher than those of Keyes and Burks by 0.05 to 0.20%. At 100, 150 and 200" agreement of the two sets of data appears satisfactory except at 60 atmospheres at 150° and at 200 and 250 atmospheres at 200°. Here the maximum deviation, which occurs at 250 atmospheres at 200°, amounts to 0.24%.

The order of taking the data presented in Table I was very irregular. In the course of a day determinations would often be made at three or four different temperatures over a comparatively small pressure range. This manner of collecting the data minimized the chance that any one isotherm might contain a constant error peculiar to itself. The regularity of the data, as a whole, attests the accuracy of the method.

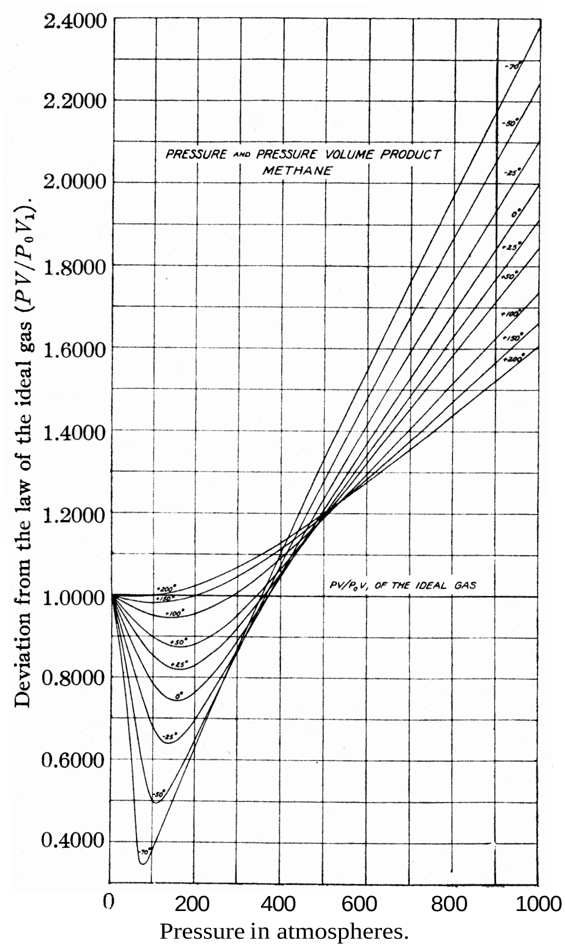

Fig. 1.

Two lines of evidence indicate that adsorption did not occur on the walls of the pipet to any appreciable extent. First, when gas was allowed to expand from the pipet at high pressure, there was no increase in the quantity of gas obtained after the outlet valve was completely opened. Second, two pipets having wall surfaces in the ratio 1:4 and volumes in the ratio 1:16 gave results agreeing to 0.05% or better at 70 atmospheres and −50" and at 80 atmospheres and −25°.

Below 100° the isotherms show great curvature at all pressures. Above 370 atmospheres this is in such a direction that the slope of the isotherm decreases with increase in pressure. The 100° isotherm is straight through the 500–1000 atmosphere range, while through this same range the slopes of the 150 and 200" isotherms increase with increase in pressure.

The "unique point' found in nitrogen[6] at 380 atmospheres and with carbon monoxide[6] at 375 atmospheres is duplicated in methane at 533 atmospheres for the 100 to 200° range. This indicates that through a certain temperature range every gas may exhibit this phenomenon. Below the "unique" temperature range the P V isotherms will deviate with decreasing temperature toward the isotherm of the gas and liquid at the critical temperature and above this range will deviate toward the isotherm of the ideal gas, becoming identical with it at infinite temperature. Hydrogen at −70° is already above the range, nitrogen is within it from 100 to −70°, while carbon monoxide is within it for the temperature interval −70 to 200°.

The authors wish to express their appreciation for the advice and encouragement received from Dr. E. P. Bartlett during the progress of this work. The range of experimental data was made possible through the cooperation of the staff of the Fixed Nitrogen Research Laboratory.

Summary

The compressibility isotherms of methane have been determined to 1000 atmospheres at nine temperatures through the range −70 to 200°. In the range of pressure and temperature duplicated, the results are in agreement with those of Keyes and Burks. With the exception of the pressure interval 500–1000 atmospheres at 100° the compressibility isotherms have considerable curvature.

WASHINGTON, D. *C*.

[CONTRIBUTION FROM THE ENGINEERING EXPERIMENT STATION AND THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

COBALTIC SULFATE AS AN OXIDIZING AGENT[1]

BY SHERLOCK SWANN, JR., AND THEODORE S. XANTHAKOS

RECEIVED JUNE 23, 1930 PUBLISHED FEBRUARY 9, 1931

Since the oxidation potential of cobaltic sulfate is the highest of any of the easily regenerated oxidizing agents which might be used as oxygen carriers in the electrolytic oxidation of organic compounds, a study of its behavior as an oxidizing agent seemed desirable.

By the use of organic compounds of varied susceptibilities to oxidation, such a study should give an indication of the feasibility of cobaltic sulfate as an oxygen carrier and should also indicate the type of oxidation for which cobaltic sulfate is best adapted. The work was undertaken with these ideas in mind.

The only reference found in a literature search where cobaltic sulfate was used as an oxidizing agent was in a paper by Conant and Aston[2] in which they showed that isobutyric aldehyde was oxidized to acetone and other products.

Experimental

At the beginning of the investigation a method for the preparation of cobaltic sulfate was sought. That which suggested itself immediately was the electrolytic method described by Erich Müller,[3] which consisted in the oxidation of cobaltous sulfate in 8 N sulfuric acid at a platinum anode. The yields obtained were not entirely satisfactory under these conditions. A study was therefore undertaken to determine the optimum conditions for the preparation in the hope of improving the yield and shortening the time required.

The apparatus consisted of a large porous cup of 800 cc. capacity as the anode compartment which was placed in an 1000-cc. beaker. A platinum sheet of 80 sq. cm. area was used as the anode while a sheet of copper of about 300 sq. cm. area on the anode side which surrounded the porous cup served as the cathode.

The anolyte consisted of 500 cc. of a saturated solution of cobaltous sulfate in sulfuric acid. The catholyte was of the same composition. In all cases a current of 5 amperes was employed. The anode current density was therefore about 0.06 ampere per sq. cm. The temperature was controlled either by a cooling coil or an ice-bath

Experiments were carried out at various temperatures and with different concentrations of sulfuric acid The results are given in the tables.

The free acid concentration was determined electrometrically. The cobaltic sulfate prepared was always in suspension in the anode liquor, which was so viscous that a sample could not be taken by means of a

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[1] Published by permission of the Director of the Engineering Experiment Station.

[2] Conant and Aston, THIS JOURNAL, 50, 2783 (1928).

[3] Erich Muller, "Elektrochemisches Praktikum," 4th ed., p. 210.

pipet. A quantitative analysis was therefore not possible. It was estimated by weight after filtration by suction through asbestos. The product was not dried further.

TABLE I

EFFECT OF TEMPERATURE

Free acid normality	Temp., °C.	Duration of oxidation in hours	$Co_2(SO_4)_3$ per 100 cc. of soln., g.
8	25	5.5	0
8	23	5.5	Very little
8	18	5.5	Very little
8	10	3.5	15
EFFECT OF FREE ACID CONCENTRATION			
8.3	10	2.75	33.2
9.55	10	3.5	47.7
10.7	10	2.5	40
11.9	10	3.67	21

This method of determining cobaltic sulfate is not accurate on account of the large amount of mother liquor retained by the crystals. The results should be comparable, however, because each determination was made in the same way.

In order to determine the effect of current density, some experiments were carried out in a much smaller cell. The method of analysis was different in this set of experiments. At the end of each run the anolyte was poured into a standard solution of $N/10$ sodium oxalate. The excess oxalate was titrated electrometrically with $N/10$ potassium permanganate. The results of these experiments are shown in the following table.

TABLE II

EFFECT OF CURRENT DENSITY ON YIELD

Amp.	Current density in amp. per sq. cm.	Duration of oxidation in hours	Yield of $Co_2(SO_4)_3$, g.
0.7	0.0088	2.75	2.48
1.0	.043	2.75	4.00
0.7	.047	2.75	3.15
1.0	.073	2.75	3.75
1.0	.180	2.75	4.40
0.7	.350	2.75	2.97

The temperature in these experiments varied between 10–13". It was noticed that the crystals of cobaltic sulfate became smaller with increase of current density until at 0.18 amp. per sq. cm. the solution could be drawn up into a pipet very readily. The optimum current density is roughly between 0.01 and 0.2 amp. per sq. cm.

Finally the current and material yields of cobaltic sulfate were determined. Since small crystals were obtained at a current density of 0.18 amp. per sq. cm., the current density used in this set of experiments was almost the same, 0.17 amp. per sq. cm. The current efficiency was determined as the oxidation progressed by an analysis of a 1-cc. sample of anode suspension drawn out by means of the pipet. The cobaltic sulfate was determined electrometrically as in the last set of experiments. The cobaltic sulfate was present in the form of fine crystals which were distributed uniformly throughout the anode liquor. The results are shown in Table III.

TABLE III

EFFECT OF DURATION OF OXIDATION ON CURRENT EFFICIENCY AND YIELD

Duration of oxidation	Amp.	Current efficiency, %	Material yield in % by wt.	$Co_2(SO_4)_3$, normality of anode suspension
1 hr. 40 min.	1	84.3	...	0.225
2 hrs. 52 min.	1	74.5	...	.415
3 hrs. 52 min.	1	63.8	(93.33)	.560
5 hrs.	1	..	...	.564

Temp., 6°. Normality of H_2SO_4, 10. Normality of $CoSO_4$, 1.2. Volume of anode solution, 100 cc. Theoretical amount of electricity, 2 faradays.

The anode liquor was always kept free from soluble organic materials since they either retarded the rate of oxidation of the cobaltous salt or prevented its oxidation.

From the results of the experiments carried out it may be shown that satisfactory conditions for the preparation of cobaltic sulfate in the apparatus described are as follows.

The solution must not be allowed to rise in temperature above 10°. The normality of free sulfuric acid should be 10. The current density may vary roughly between 0.01–0.2 amp. per sq cm.[2] Higher current densities cause the product to form in smaller crystals than in the case of lower current densities. Not more than a five-ampere current should be employed for 500 cc. of anolyte; otherwise the temperature cannot be controlled. The cobaltic sulfate precipitates out in the form of greenish-blue crystals on account of its insolubility in the strong sulfuric acid. The maximum yield will be obtained at the end of four hours.

Oxidations with Cobaltic Sulfate.—In order to estimate the strength of cobaltic sulfate as an oxidizing agent, it was tried with the following organic compounds of varied susceptibilities toward oxidation: amylene, benzene, ethyl alcohol and acetic acid.

It was thought that cobaltic sulfate might be used to best advantage as an analytical reagent to oxidize certain organic compounds to carbon dioxide quantitatively rather than as an oxidizing agent in preparations because too large quantities were necessary on account of its high molecular weight. With this idea in mind the following compounds were studied: acetone, glycerin, ethylene glycol, and formic, tartaric, citric and malic acids.

Apparatus and Procedure

For the oxidations to test the oxidizing power of cobaltic sulfate a shaking machine was set up, holding an Erlenmeyer flask of 500-cc. capacity which could be surrounded by an ice–salt bath.

The organic compound to be oxidized was placed in the flask with the cobaltic sulfate suspension just as formed in the anode compartment of the cell. A rubber stopper was inserted containing a rubber tube leading to a gas-collecting bottle filled with water. The flask was surrounded by an ice–salt bath and was then shaken for two to three hours. At the end of that time it was found that oxidation had taken place and the green suspension had turned to a pink solution. The gas was analyzed for carbon dioxide and the solution steam distilled after the removal of insoluble material.

The steam distillate was neutralized with standard sodium hydroxide, evaporated to dryness and the salt weighed. The salt was dissolved in water and less than the theoretical quantity of sulfuric acid was added to liberate any organic acid. Sufficient water was used to obtain a solution of 1 to 2% of free organic acid. This was distilled away from the sodium sulfate and a Duclaux[4] test run.

The procedure for the complete oxidations was not the same. In this case the apparatus and procedure of Franz and Lutze[5] was followed.

The organic compound to be oxidized was placed in a three-necked flask equipped with a stirrer. In one neck was placed a glass tube leading to the bottom of the flask and drawn out to a capillary. This was connected by rubber tubing to a soda lime tower. The tubing could be closed by a screw clamp. The soda lime tower was connected to the air line. The other neck of the flask was connected to a train consisting of a wash bottle containing water, a large calcium chloride tower, an anhydrone tower and an ascarite tube in the order named.

A weighed amount of the organic compound was placed in the flask with the cobaltic sulfate suspension. Liquids were washed in with a little water and the connection to the air line shut off. The stirrer was started and the oxidation was allowed to proceed for about an hour. The air line was then opened and a slow stream of air was allowed to bubble through the liquid in the flask for half an hour while the flask was heated by a water-bath. The ascarite tube was weighed and the percentage of carbon dioxide calculated.

In the preparations of cobaltic sulfate for these runs it was found that the yields were practically identical if the conditions were always the same. Therefore, no determination of the amount of cobaltic sulfate in the suspension was made. It was assumed that the same quantity was present in every run. The results of the investigation are given in Table IV.

TABLE IV

RESULTS AND CONCLUSIONS

	CO_2, %	Aldehydes	Acids	Moles of compound	Moles of $Co_2(SO_4)_3$
Amylene (mixture)	0	Trace	Formic and others	0.422	0 14
Benzene	0	Phenolic	Compounds	5	14
Acetic acid	0 2	.....	....	75	.14
Ethyl alcohol	4 08	Considerable	Considerable acetic	0164	14
Acetone	13	None	Considerable acetic	0149	14
Glycerine	0	None	Considerable formic	0274	14
Ethylene glycol	96 05			0099	14
Formic acid	99.96			0205	14
Tartaric acid	101.22	..	....	00099	11
Citric acid	99.87	..	....	000745	14
Malic acid	100.3	..	....	001368	14
Malic acid	73.2			002543	14

The amount of product from the oxidation of benzene was insufficient for purposes of identification. Phenolic compounds were shown to be present by their odor.

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[4] Kamm, "Qualitative Organic Analysis," 1923, p. 139

[5] Franz and Lutze, Rer., **57B,** 768 (1924).

The results of the oxidation of amylene, benzene, ethyl alcohol and acetic acid show that cobaltic sulfate behaves as a strong oxidizing agent and should be an excellent oxygen carrier for anodic oxidations in cases where no interference with its formation occurs.

It may seem strange that while formic acid is completely oxidized when no other compounds are present, it remains unoxidized in the presence of amylene and glycerin. This may be explained by the fact that formic acid might be more difficult to oxidize than the other two compounds in strong acid. Hatcher and West[6] found formic acid in the oxidation of malonic acid by acid perrnanganate. They showed that the rate of oxidation of formic acid was inversely proportional to the PH of the solution. The Duclaux test was carried out with great care and it is not believed that the information from it is misleading.

The results of the experiments on complete oxidation indicate that cobaltic sulfate may be used in the same manner as persulfates for types of compounds which are easily oxidized to carbon dioxide.

In all cases where cobaltic sulfate is used as an oxidizing agent most of it decomposes to yield free oxygen. Rapid decomposition sets in even at low temperatures. The organic compound seems to catalyze this decomposition. Consequently for complete oxidations it is necessary to use very large quantities of cobaltic sulfate. It is used, therefore, to best advantage as an analytical reagent and not for the purpose of oxidizing large quantities of material.

Summary

1. **A** study of the electrolytic preparation of cobaltic sulfate has been carried out.

2. The behavior of cobaltic sulfate as an oxidizing agent for organic compounds has been studied. It has been shown that cobaltic sulfate is a strong oxidizing agent. It may be used as an analytical reagent for oxidizing certain compounds quantitatively to carbon dioxide.

URBANA, ILLINOIS

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[6] Hatcher and West, *Trans. Roy. Soc.*, **3,** 21 [Sec. 3], **269 (1927).**

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

THE PHOTOCHEMICAL DISSOCIATION OF TRIATOMIC MOLECULES. II. POTASSIUM CYANIDE

BY DONALD STATLER VILLARS

RECEIVED JUNE 24, 1930 PUBLISHED FEBRUARY 9, 1931

In a previous article[1] the dissociation energetics of hydrogen cyanide were investigated and it was found that if this molecule were of an atomic binding, as are the corresponding hydrogen halides, one should not expect it to have a continuous absorption spectrum in an energy region less than 6.2 volts ($\lambda > 1990$ Å.). This was verified experimentally. The next molecule chosen for investigation was potassium cyanide. This should be more amenable to experimentation, if one may infer an analogy between the corresponding cyanides and halides.

The Heat of Dissociation of Normal Potassium Cyanide.—The *atomic* heat of formation (Q_A) of potassium cyanide (the heat of formation from the gaseous atoms) may almost be estimated from data in the "International Critical Tables."

$$\begin{aligned} \text{KCN (c)} + Q + L_{S_K} + L_{S_C} + {}^1/_2 D_{N_2} &= \text{K} + \text{C} + \text{N} \qquad (1)\\ \mathbf{1.2} + 0.9 + \mathbf{6.4} + 4.8 &= \mathbf{13.3}\text{ v} = Q_{A-\text{KCN(c)}} \end{aligned}$$

From this value must be subtracted the heat of sublimation, L_S, to get the atomic heat of formation of gaseous potassium cyanide. This is not known but an estimate may be obtained by a method to be described below.

$$Q_{A-\text{KCN(g)}} = \mathbf{13.3}\text{ v.} - L_S = E_1 \qquad (2)$$

When we consider the four possible dissociation combinations as in the previous work, we find we have the heat of formation of CN but not that of either KN or KC. However, we shall assume that the stability of such unsatisfied (as to valence) molecules is quite small, especially as their band spectra are not known, and, if this is so, such modes of dissociation should occur relatively infrequently when compared with the process

$$\text{KCN (g)} + E_2 \longrightarrow \text{K} + \text{CN} \qquad (3)$$

The energy, E_2, then is

$$\begin{aligned} E_2 &= \mathbf{13.3} - L_S - \mathbf{7.3}\text{ v.}\\ &= 6.0 - L_S \qquad (4) \end{aligned}$$

Experimental

The apparatus was of the same type as that used in the investigation of hydrogen cyanide, with the exception of a small Gaertner quartz spectrograph which was used instead of an E_1 Hilger. Although the dispersion of this instrument is much less (the whole spectrum of visible and ultraviolet is spread over a distance of about 105 mm.), nevertheless, this proves to be an advantage as the light strength of the instrument is so much the

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[1] Villars, THIS JOURNAL, 52, 61 (1930), hereafter designated as I.

greater. The hydrogen arc (initial pressure of hydrogen 1.45 mm.) was run at about 0.55 ampere and 3500 volts and exposures of five and ten minutes were made. The potassium cyanide (Baker's 96–98% pure; SO_2, 0.05%; Cl, 0.25; org. matter, trace) was placed in the quartz tube adjacent to the constriction leading to the quartz absorption cell and after evacuating and outgassing the latter the cyanide was heated to distil it over into the cell. It melted quite readily and the liquid boiled (pressure 10^{-4} mm.), at the same time turning black. The distillation did not take place very readily, but several drops of the melt were pushed bodily across the constriction. The cell was sealed off and the isolated product had a clear transparent appearance with a reddish tint. No liquid-air trap was used during the evacuation process. The potassium compound was quite ruinous to the cell at high temperatures (1050°) as it caused such a rapid devitrification of the quartz that it fell to pieces shortly after cooling to room temperature.

A possible objection which might be made to the present work is that the spectra observed do not come from potassium cyanide, but from potassium hydroxide which might have been left behind as an hydrolysis product after the evacuation. Before the cyanide was sealed off, it had absorbed an appreciable amount of water during the glass blowing. This objection is overthrown by two considerations. First, an analysis of the residue showed that, within titration errors, there was no potassium hydroxide present. Second, it has been shown in a subsequent research, which will be reported later, that potassium hydroxide has to be heated to a much higher temperature before it will reach a vapor pressure great enough to absorb.

Results

Figure 1 gives the microphotometer record of the hydrogen source transmitted by the cell at room temperature (no absorption). The banded structure is due to the impurities in the lamp, the latter being only newly broken in. Figure *2* gives the record of the absorption at about 830° and Fig. 3 that at 875°. It is seen that, at this latter temperature, there are two regions of absorption. A visual study of the original plate indicated that the long wave length limits of these two regions are 2175 and 2900 Å., which correspond, respectively, to 5.7 and 4.3 volts, the difference being 1.4 v.

Since the difference of 1.4 v. is, within the errors of measurement, equal to the excitation energy of CN (1.8 **v.)** or K (1.6 v.), it is indicated that the photochemical dissociation process requiring least energy is the one resulting in normal products. This conclusion is not yet inescapable for the following reasons. If the longest wave length limit of continuous absorption should be at an energy corresponding to dissociation into a normal and an excited product, the next continuous absorption region should correspond to dissociation into a product in the next higher excited state. These energies would be in the following steps: K' (1.6), CN' (1.8), K" (2.71, CN" (3.21, K' + CN' (3.4), etc. Granting that in the roughness of the measurement the two expected regions spaced by 0.2 v.

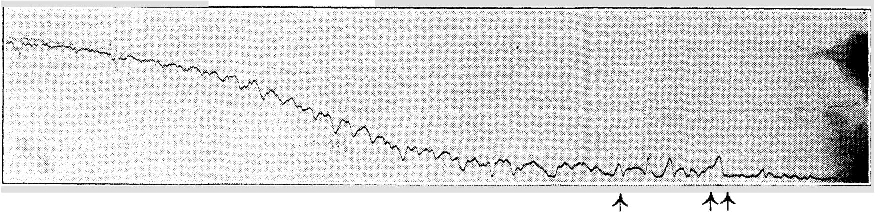

Fig. 1.—Plate M8, H_2 lamp, five minutes, cell at room temperature.

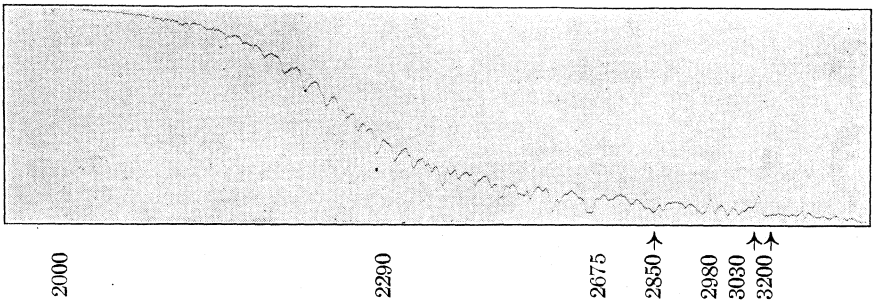

Fig. 2.—Plate M8 KCN, 790–870°.

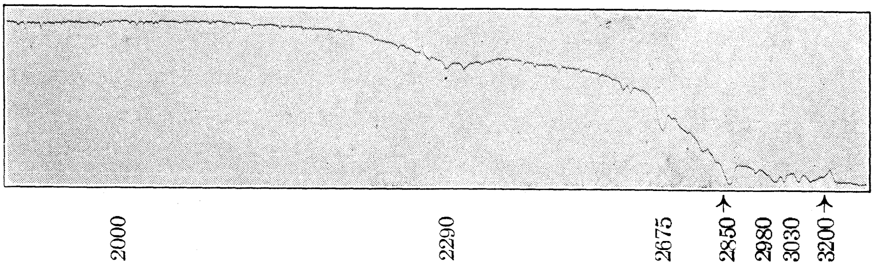

Fig. 3.—Plate M8 KCN above 875".

(K' and CN') are indistinguishable and that the one 1 v. farther on (K") has too low an intensity, the next one (CN") is at the experimentally observed distance from the first two (1.5 v.). One could decide for or against this possibility if he knew the heat of sublimation of potassium cyanide. For, if the first photochemical act were a dissociation into two *normal* products the energy, E_2, should exactly equal the energy corresponding to the convergence limit of continuous absorption (4.3 v.).

If the act were a dissociation into a normal and an excited product, the longest wave length limit should correspond to $E_2 + 1.6$ v. (or $+ 1.8$).

Although there are no measurements given of the heat of sublimation of potassium cyanide, an estimate may be obtained by making use of the third law. We know that, in order to absorb light, the vapor pressure must reach a value of the order of magnitude of 1–10 mm. Absorption not setting in until a temperature of 870° was reached, we shall assume the vapor pressure at this temperature to be 1 mm. Now if we can know the entropy of crystalline and gaseous potassium cyanide at that temperature we can calculate from the free energy of sublimation the heat of sublimation by the equation

$$AF = AH - TAS = -RT\ln K = -RT\ln p\text{ vapor} \qquad (5)$$

$$\log p_{\text{atm.}} = -\Delta H/4.575T + \Delta S/4.575 \qquad (6)$$

Latimer[2] has shown that the entropy of diatomic solids may be well represented by the sum of "atomic" entropies

$$S^\circ_{298\text{ solid}} = (3/2)R\ln A - 0.94 \qquad (7)$$

If we treat potassium cyanide as a diatomic molecule, counting 26 as the atomic weight of CN, we get

$$S^\circ_{298\text{ KCN (c)}} = 18.73\text{ E. U.}$$

Latimer's equation for the entropy of a diatomic gas

$$S^\circ_{298\text{ gas}} = R\ln(w^{3/2}A_1^{1/2}A_2^{1/2}) + 30.22 \qquad (8)$$

gives

$$S_{298\text{ KCN (g)}} = 49.58$$

and

$$\Delta S_{298} = 30.85$$

Correcting for temperature, we have

$$\begin{aligned}\Delta S_{1143} &= 30.85 + 3R\ln T/298 - (5/2)R\ln T/298 \\ &= 29.51 \qquad (9)\end{aligned}$$

Substituting these values in Equation 6 above and using for the pressure 0.00132 atm. we get AH = 48.75 kg. cal. = 2.1 v. = L_S. Therefore, $E_2 = 5.9 - 2.1 = 3.8$ v., which agrees very well with the observed long wave length limit of continuous absorption of (4.3 v.). It should be emphasized here, before passing on, that our estimate of the entropies of solid and gaseous potassium cyanide is extremely crude and for that reason the calculated value of E_2 is subject to considerable error.

From the above we see that, on the one hand, if the first photochemical act were dissociation into a normal and an excited product, the heat of dissociation into normal products would be approximately $4.3 - 1.6 = 2.7$ v., which corresponds to a heat of sublimation of $L_S = 6.0 - 2.7 = 3.3$ v. (= 74 kg. cal.). This requires, if our A S is correct, a vapor pressure of 10^{-5} mm., which is not enough for absorption. On the other hand, if the first act is a dissociation into normal products and we go to the

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[2] Latimer, THIS JOURNAL, **43,** 818 (1921).

extreme of taking the observed value of 4.3 v. for E_2 (a value which does not necessarily follow as the convergence limit of the absorption series was not actually observed), this gives a heat of sublimation of L_S = 6.0 − 4.3 = 1.7 v. (= 37 kg. cal.), which corresponds to a vapor pressure of 170 mm., much nearer the correct order of magnitude to account for light absorption in a cell only some 77 mm. in length.

Validity of the **Franck–Kuhn**[3] Criterion of Atomic and Ionic Binding.—It has been pointed out recently by Sommermeyer[4] that the test proposed by Franck and Kuhn[3] as a distinction between an ionic and an atomic binding is not definitive and is rigorous only when an atomic binding is indicated. This is because of the discovery by Herzberg[5] and Heitler[6] of a *second class* of atomic molecules, the *normal* state of which dissociates on vibration into a normal and an excited product. Thus, the thermal dissociation of normal CN (convergence limit at 9.5 v.) is supposed by Mulliken[7] to result in a normal ^3P carbon atom and an excited ^2D nitrogen atom. CN excited 1.8 v., however, dissociates into two normal atoms (convergence limit 8.6 v. above normal state of molecule). The potential energy curves of the *first class* of atomic molecules are represented in Fig. 4, while those of the new *second class* are represented by Fig. 5. Rigorously, when the longest wave length convergence limit is at an energy equal to the heat of dissociation into *normal* products, it means that the molecular state which dissociates into atoms on vibration (atomic binding) is an excited state of the molecule. Our data show that this obtains in potassium cyanide vapor, but are not sufficient to define whether it is a second-class molecule of atomic binding or a molecule of ionic binding. We may be reasonably certain, however, that it is an ionic molecule, first because the only second-class atomic molecules known are those having unsatisfied

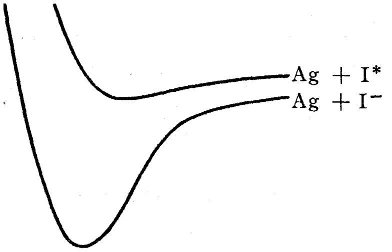

Fig. 4.—Potential energy curves for first-class atomic binding.

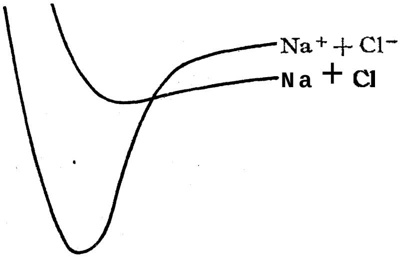

Fig. 5.—Potential energy curves for second-class atomic binding and ionic binding.

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[3] Franck and Kuhn, Z. *Physik*, 43, 164 (1927).

[4] Sommermeyer, *ibid.*, 56, 548 (1929).

[5] Herzberg, Ann. *Physik*, 86, 189 (1928).

[6] Heitler and Herzberg, Z. *Physik*, 53, 52 (1929).

[7] I. Refs. **13** and 14.

free valences, and second because the crystal structure[S] of potassium cyanide is the same as that of rock salt and presumably of an ionic nature. In general, the potential energy curves of ionic molecules cross in the same way as do those of second class atomic molecules (Fig. 5). This must be so if the data on electron affinities of the halogens are correct, for they are usually less (~ 3.5–4.5 v.) than the ionization potential of the metal (5.12, Na; 7.5, Ag; 4.3, K; etc.). This is not a necessary condition for validity of the principle that the first photochemical dissociation act (the one requiring least energy) of an ionic molecule will result in normal products. It makes no difference whether the ionic binding curve crosses the atomic binding one or not. Although at the end of the curve for NaCl (Fig. 5) the dissociated state, $Na^+ + Cl^-$, is higher than the one, Na + Cl, still we cannot expect to find an extra continuous absorption region corresponding to dissociation into the former products, because it belongs to the same potential energy curve as the initial (absorption) state and such large changes in vibrational quantum number with no change in electronic quantum number not only are not known, but they violate the Franck–Condon principle.

The change with temperature in the relative stability of the ionic and atomic forms of silver iodide postulated by Franck and Kuhn[3] is due, we should like to suggest, not to a variation in shape of the curves for different temperatures (they must necessarily be independent of temperature) but to the variation of the free energy of the reaction

$$\text{Ionic} \rightleftharpoons \text{Atomic} \tag{10}$$

From Equation 5 may be obtained[9]

$$\Delta F = D_0 - T A S' \tag{11}$$

where D_0 is the heat of reaction (absorbed heat) at the absolute zero and[10]

$$S'_{\text{rot.}} = R \ln 8r^2 IkT/h^2 \tag{12}$$

$$S'_{\text{vibr.}} = -R \ln (1 - e^{-\epsilon/kT}) \tag{13}$$

Thus

$$AS' = R \ln I_A (1 - e^{-\epsilon_I/kT})/I_I(1 - e^{-\epsilon_A/kT}) \tag{14}$$

$$\longrightarrow R \ln I_A \epsilon_I/I_I\epsilon_A \text{ for } \epsilon << kT$$

$$\longrightarrow R \ln I \qquad \text{ for } \epsilon >> kT$$

Since the moment of inertia in the atomic bound molecule is presumably larger and the vibrational quantum smaller, AS' is positive and therefore A F will vary from a positive quantity at O°K. (= D_0) to a negative quantity at very high temperatures. This corresponds to the behavior postulated by Franck and Kuhn of the ionic and atomic forms of silver iodide. If this suggestion is valid, it seems that it should be possible, by going to still higher temperatures, to find one above which the atomic form of sodium chloride is in greater abundance than the ionic form.

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[8] Bozorth, THIS JOURNAL, 44, 317 (1922); Cooper, *Nature*, 110, 544 (1922).

[9] Villars, *Proc. Nat. Acad. Sci.*, 15, 705 (1929); 16, 396 (1930).

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

Summary

Potassium cyanide vapor at 875° absorbs light in two regions, the long wave length boundaries of which are approximately 2175 (5.7 v.) and 2900 Å. (4.3 v.). The latter absorption region is interpreted, according to Franck, Kuhn and Rollefson, as representing dissociation of the ionic molecule into a normal potassium atom and a normal CN radical and agrees within 0.5 v. with the calorimetric data, supplemented by an estimate of the heat of sublimation (48.8 k. cal.). The former absorption act takes place at an energy 1.4 v. greater and represents dissociation into a normal and an excited dissociation product (K excitation 1.6; CN, 1.8 v.). The change with temperature in stability of the two molecular forms postulated by Franck and Kuhn is explained in the light of the free energy.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES.[1] III. THE DESIGN OF CELLS

BY GRINNELL JONES AND GILES M. BOLLINGER

RECEIVED SEPTEMBER 22, 1930 PUBLISHED FEBRUARY 9, 1931

Historical Introduction

In 1923 H. C. Parker[2] published two papers which challenge a fundamental postulate of the Kohlrausch method for the measurement of the conductance of electrolytes, by the observation that "cell constants" are apparently not really constant but vary with the resistance being measured. If a solution of specific conductance, κ, is placed in a cell, A, whose length is l and whose cross section is a, then the fundamental premise of the Kohlrausch method is that the resistance, R_A, is given by the equation

$$R_A = \left(\frac{l}{a}\right)_A \frac{1}{\kappa} \qquad (1)$$

$(l/a)_A$ is designated as the "cell constant"[3] and has been assumed to have a fixed value for any given cell at a given temperature, and this assumption is vital for the Kohlrausch method.

If we have two different cells, A and B, and fill them with the same solution and designate the corresponding resistances and cell constants by

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[1] The first two papers in this series are: Grinnell Jones and R. C. Josephs, THIS JOURNAL, 50, 1049 (1928); Grinnell Jones and Giles M. Bollinger, ibid., 51,2407 (1929).

[2] H. C. Parker, ibid., 45, 1366, 2017 (1923).

[3] If the cross section is not uniform the cell constant is $\int_0^l \frac{dl}{a}$.

suffixes, we may eliminate the specific conductance of the solution used giving

$$\frac{R_A}{R_B} = \frac{(l/a)_A}{(l/a)_B} \tag{2}$$

Therefore, if Equation 1 is valid, the ratio of the resistances of any pair of cells when filled with the same solution should be the same as the ratio of the cell constants, and should be independent of the composition and concentration of the solution used and hence of the resistance being measured. This ratio should also be independent of the frequency and the voltage used in the measurements.

Parker compared the resistances of two cells, sealed together so as to facilitate filling them with a common solution, and found that the ratio of the resistances, instead of being constant, varied in a complicated but systematic manner with the specific conductance of the solution chosen for the comparison. Parker has recorded data and drawn curves for seven cases. In these curves the ratios of the resistances are plotted as ordinates and the resistances of the cell having the lower cell constant as abscissas. The lines depicting the resistance ratio, instead of being horizontal and straight, have a varied shape. All show a steep negative slope at low resistances. Three of his curves show both a maximum and a minimum, two a minimum but no maximum, and two show a gentle negative slope at high resistances but no maximum or minimum. The phenomena are evidently very complicated. He has not determined the influence of variations in frequency on the cell resistance ratios. Although the variations are apparently exaggerated in his figures because the zero on the ordinate scale is not shown, the variations are substantial. In one case recorded by Parker the deviation amounts to 0.33%. If, as seems probable, the errors in the two cells are in the same direction, this figure is the difference in the errors, and the actual error in using Equation 1 may be greater by a considerable and unknown amount. All measurements were made with solutions of potassium chloride.

Parker regards polarization as the cause of the steep negative slope of these curves at low resistances. He is doubtless correct in this interpretation although he makes no attempt to show that the shape of his curves is in conformity with the known facts about polarization. In view of the earlier literature on polarization this interpretation lacks novelty.

On the other hand, Parker appears to have been the first to observe the more gentle and usually positive slope of these curves at resistances above the range in which polarization predominates. At any rate he was the first observer with the courage to record his data, and we shall therefore call this anomaly the Parker Effect to distinguish it from polarization. This positive slope at moderate resistances is ascribed by Parker to adsorption of electrolyte at the electrodes, although the arguments in favor of this suggestion are extremely weak. He is unable to account for the peculiarities of his various cases by the aid of this hypothesis. He offers no explanation of the appearance of a maximum and a negative slope at very high resistances and gives it little consideration because it does not appear in all of his cases.

Randall and Scott[4] have confirmed the existence of the Parker Effect. They used a single pair of cells only, not sealed together, and a single frequency (1000 cycles), but used four electrolytes, potassium chloride, barium nitrate, sodium sulfate and sulfuric acid. For potassium chloride their results are similar to those of Parker. The steep negative slope at low resistances, which Parker ascribed to polarization, is absent for the other three electrolytes. The Parker Effect, represented by a positive slope of the resistance ratio curves, was obtained with barium nitrate as well as with potassium chloride. They concluded from their experiments that the Parker Effect is absent in the case of sodium sulfate and sulfuric acid and regarded this alleged difference in behavior of these electrolytes as supporting the hypothesis advanced by Parker that adsorption is the cause of the phenomena since it is characteristic of adsorption to vary greatly in different cases. It should be noted, however, that when the cells were filled with sulfuric acid and with sodium sulfate, measurements at high resistances were omitted. Whereas with potassium chloride the highest resistance measured in the longer cell was about 64,000 ohms, when using sulfuric acid the upper limit was only 5100 ohms, and, therefore, these experiments do not prove that the curves might not have been similar if comparable resistances had been used. In the case of sodium sulfate the upper limit was about 31,000 ohms, a little less than half that used with potassium chloride. The result with this most dilute solution does show a rise of about 0 10%; nevertheless this rise is ignored by Randall and Scott in drawing their curves and in the interpretation of their data. Randall and Scott offer no reason for ignoring the evidence of their data on the highest resistance they measured or for not extending the measurements on sodium sulfate and on sulfuric acid to as high resistances as were used with the other salts. The only suggestion for a remedy of the Parker Effect that they offer is that sodium sulfate would be a better substance than potassium chloride for standard solutions for the determination of cell constants. But this suggestion, even if it were based on unquestionable premises, would not give a means of obtaining accurate conductance data if adsorption of the salt being measured can cause an error.

Some recent experiments by F. A. Smith[5] are of interest as an extreme example of the Parker Effect. His cell contained three electrodes consisting of coaxial cylinders open at the ends, two of which were concentric and

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[4] M. Randall and G. N. Scott, THIS JOURNAL, 49,636 (1927).

[5] F. A. Smith, *ibid.*, 49, 2167 (1927).

close together and the third at some distance from the others, presenting its edge to an edge of the others. By using the two electrodes positioned close together, a cell of low cell constant was available, and by using one of the close electrodes and the distant electrode a second cell having a cell constant about two hundred times greater was available. Smith's data afford comparison between two cells of widely different cell constant, covering a great range in concentration and extending to very high resistances under conditions that insure identity of composition of the solution in the two cells. Smith reports a change in the apparent cell constant ratio between the most concentrated solution and the most dilute amounting to more than 50%. This is an extreme case of the Parker Effect. Smith reports such data on three cases, ammonium chloride dissolved in liquid ammonia, ammonium nitrate dissolved in liquid ammonia, and potassium chloride in water. The data on these three cases, when plotted as resistance ratio against resistance in one cell, all fall on the same curve. This creates a presumption that the cause of the effect is purely electrical, rather than due to adsorption. If the effect is to be explained as due to adsorption it will have to be maintained that the adsorption in these three cases and the variation thereof with the concentration cause an identical effect on the conductance, which is hardly plausible. Smith used a single frequency of 1000 cycles only. His cells were closely shielded and without proper grounding of the bridge, which probably contributed to the very large errors, so that errors of this magnitude are not to be regarded as common or unavoidable.

O. Redlich[6] has devised a radically different method of measuring conductance in an effort to avoid errors due to electrode processes (polarization, adsorption, etc.). His apparatus may be regarded as a double alternating current potentiometer instead of a Wheatstone–Kohlrausch bridge. His cell contained three platinized platinum electrodes of the usual type which served as current electrodes, and near each a small platinum potential electrode through which no current flows when the measurements were being made. With a given solution in the cell he made measurements by the Kohlrausch method between three pairs of large electrodes and also by his new method between three pairs of small electrodes. The solution was replaced by another of different specific conductance and the measurements repeated. In this way several cell resistance ratios were compared using two radically different methods of measurement. He varied the specific conductance of the solution used by about ninetyfold and when using the large electrodes and the Kohlrausch method found no variation in cell constant ratio greater than 0.03%. Just what difference in cell design or bridge design or manipulation as compared to Parker's is responsible for the comparatively small Parker Effect in his experiments is

[6] *O.* Redlich, *Z. physik.* Chem , 136,331 (1928).

not discussed by Redlich and is not immediately obvious. So long as the resistances being measured did not exceed 2300 ohms the results by the new method agreed with those of the older method within about 0.03%. At higher resistances discrepancies up to 0.1% occurred.

Recently Shedlovsky[7] has designed, built and tested a new form of cell intended to eliminate any effects at the electrodes which would disturb conductance measurements, especially polarization and adsorption. In Shedlovsky's cell the two end electrodes, which carry the current and are subject to electrode effects, were in different adjacent arms of the bridge and hence electrode disturbances tended to compensate each other. The midpoint of the bridge was inside the cell itself and consisted of a loop of fine smooth platinum wire. Since the loop composing the midpoint was nearer to one of the end electrodes than to the other, the difference of the resistance of the portions in the two arms had to be balanced by a resistance box in the same arm as the short portion of the cell. Shedlovsky provided three different midpoint loops at different positions which could be used in turn. He made measurements at three different frequencies, 1000, 2000 and 3000 cycles. He filled his cell with four different solutions (0.005 *N* KCl, 0.001 N HCl, 0.002 N HCl, 0.004 N HCl) and on each filling measured each electrode combination at each of his three frequencies. By subtracting the readings obtained by the use of the three different loops he attempted to eliminate the electrode effects entirely. Although the individual readings show deviations from the mean up to a maximum of 0.08%, the results indicate that the differences obtained as described above are probably reliable to within 0.01%. It should be pointed out, however, that the specific conductance of the solutions used in these tests only covered a fourfold range, so that the test was not as severe as if a wider range had been used. This range is inconveniently small for the practical use of the cell. The necessity of taking multiple readings and subtracting the results is a disadvantage in the routine use of the cell; nevertheless Shedlovsky's cell is evidently a distinct step in advance in eliminating polarization and other electrode effects. It would be interesting to have

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[7] T. Shedlovsky, THIS JOURNAL, 52, 1806 (1930). During the course of our experimental study of the problem we learned that Dr. Theodore Shedlovsky of the Rockefeller Institute for Medical Research in New York was engaged in a study of the same problem. We have kept in touch with each other's work by occasional visits and frank discussion and correspondence while attacking the problem along different lines Dr. Shedlovsky's paper has been published after the completion of our experimental work but before the completion of our manuscript. We wish to compliment Dr Shedlovsky on his literary skill in writing his paper so as to embody only ideas already in the literature and his own new ideas with a complete exclusion of ideas based on our work which we had disclosed to him in advance of publication. Since Dr. Shedlovsky's paper has now been published it is not necessary for us to attempt the same difficult task, but we cordially acknowledge Dr. Shedlovsky's priority on all points covered in his recent paper on cell design.

data obtained with the Shedlovsky cell on concentrated solutions in which polarization is a more serious difficulty.

It is evident that the Parker Effect, unobserved or at least unreported until 1923, throws suspicion on the data on the conductance of electrolytes obtained by the Kohlrausch method. The work cited above appears to show that the concept of a fixed and definite cell constant is invalid. Although there is no certain criterion for estimating the magnitude of the error, since the method of intercomparison of cells shows only the differences in the errors in two cells and not the absolute error in either, it is evident that errors up to at least 0.3% are likely to be present with cells of the type commonly used in spite of precautions which eliminate errors due to polarization. In one case with a cell of unusual design an error of 50% was reported. Moreover, there is no adequate theory to account for the error or errors. The hypothesis that adsorption is responsible fails to account for the known facts and has not suggested to anyone a practical remedy.

The general consistency of the data in the literature makes it seem improbable that errors of as much as 0.3% are commonly present in the results of the more careful and experienced investigators. This may indicate that some faulty detail of design may have aggravated the error in the cases cited above. But an adequate understanding of the nature and causes of the Parker Effect is urgently needed to permit an estimate of the reliability of the great mass of data now available, and, more important still, to guide the design of cells which may be relied on to have a fixed and definite cell constant.

The Determination of Phase Displacement in Conductance Cells.—All of the earlier experimenters on the Parker Effect, except Shedlovsky, have been content to use a single frequency, but our experience in the study of the errors in the bridge made it probable that the study of the influence of variations in frequency would be a great aid in understanding the nature of the phenomena. Accordingly, at least two frequencies were used in each case except in some of the preliminary trials.

Although nearly all experimenters on conductance since the time of Kohlrausch have used a capacitance in parallel with the resistance box to obtain a sharp balance, very few have recorded these capacitance readings, C_P, or made any attempt to interpret them. This is doubtless due to the fact that there was so much reactance in their circuits outside the cells (such as inductance in a helically wound slide wire, capacitance and inductance in the resistance boxes and in the bridge, and capacitance introduced by shields) that the capacitance required to obtain a balance did not depend solely or even largely on the reactance in the cell itself and, therefore, it was not to be expected that the parallel capacitance required could be correlated with the design of the cell, the frequency, specific conductance, or chemical nature of the solutions used. Some of the investigators of polarization in cells, beginning with Wien, have obtained significant information from the study of the reactance in their cells, but none of the experimenters on the Parker Effect has published the capacitance required to obtain a balance. Our bridge was designed to avoid inductance and capacitance as much as possible and it was therefore hoped that the capacitance required in parallel with the resistance box would depend primarily on the reactance in the cell and give a clue to the nature of the error responsible for the Parker Effect. We, therefore, recorded the capacitance required to obtain a balance in each of the readings, by the use of a calibrated condenser in parallel with the resistance box. The precision of these capacitance readings was much less than the precision of the resistance readings because the capacitance in most cases was very low (commonly under 100 micromicrofarads at resistances over 1000 ohms, where the Parker Effect becomes serious, and in some cases it was even below 5 micromicrofarads) and because the bridge was not designed as a capacitance bridge; nevertheless, the results did prove to be helpful in the interpretation of the data.

Since the phase displacements in the ratio arms of the bridge have been made as nearly equal as possible, we can regard the phase displacement, θ, in the arm of the bridge containing the resistance box and parallel condenser as equal to the phase displacement in the cell itself.[8] This can be computed from the well-known formula for a parallel combination of resistance and capacitance

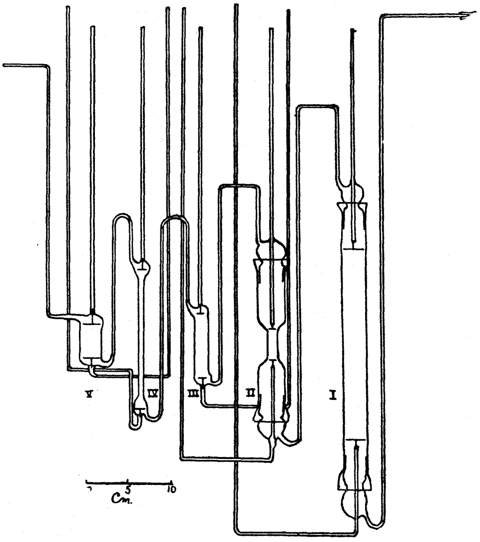

Fig. 1.—Pipet type cells, I–V.

$$\tan \theta = C_P \omega R \tag{3}$$

where f is frequency in cycles per second and $\omega = 2\pi f$.

Five cells differing greatly in design were selected or especially built and sealed together by their filling tubes, as had been done by Parker, to facilitate filling them with a common solution. These cells are shown somewhat diagrammatically in Fig. 1. Cells I, II, III had approximately the same cell constants but differed greatly in dimensions. The electrodes in cells I and II were made interchangeable by means of ground joints

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[8] Grinnell Jones and R. C. Josephs, THIS JOURNAL, 50, 1070 (1928).

These joints were very carefully ground and made perfectly tight by means of a trace of pure, soft paraffin around the outer edge. The upper joints were protected from the oil by a layer of mercury and the lower joints by the air trapped under the rim. Cells IV and V differed greatly in dimensions and cell constants from the others. The dimensions of these cells are shown in Table I.

TABLE I

CELL DATA

Dimensions of the cells used in the cell comparisons

Cell	Cell constant	Area of electrode, sq. cm.	Distance between electrodes, cm.	Diam. of tube, cm.	Platinization data			
					Light		Heavy	
					Milliamperes per sq. cm.	Min.	Milliamperes per sq. cm.	Min.
I	4.39	3.8	20	2.2	7.9	20	25	75
II	4.29	0.8	3	1.0	6.2	19	31	25
III	4.32	1.5	7	1.4	...	...	...	...
IV	51.47	2.0	16	0.5	4.0	22.5	22.5	40
V	1.232	3.1	4	2.5	6.5	20	30	45

If adsorption plays a significant part in the Parker Effect, it would be expected that lightly platinized electrodes should give less Parker Effect than heavily platinized electrodes. We, therefore, determined to make a series of measurements to test the Parker Effect with light platinization, and then give the cells a heavy platinization and repeat the measurements. But in order to have a fixed standard of reference, cell III was given a heavy platinization in advance and remained unaltered during both series. The other four cells were treated with aqua regia to remove an old platinization and were then given a light platinization using a solution of platinum chloride and hydrochloric acid (with no lead acetate) as shown in Table I. At this stage the platinization was so slight as to be barely perceptible to the eye as a slight tarnish or dimming of the bright electrode. The first series of measurements on cell resistance ratios was then carried out. For this purpose a potassium chloride solution of suitable concentration was prepared in a large "Non-Sol" bottle and thence forced into the five cells in series by compressed air. The cells were filled and emptied repeatedly to ensure thorough rinsing. In order to avoid changes in concentration of the solution by evaporation, the air used was first bubbled through some of the same solution before it entered the stock bottles. The cells were then placed in the thermostat and, after waiting for at least one-half hour for temperature equilibrium, the resistance of each cell was measured with 1090 cycles and with 2280 cycles. The capacitance required across the box in the other arm of the bridge to secure a balance was also determined from the reading of the condensers and recorded for each measurement. The solution was then replaced by a more concentrated solution and the measurements repeated. Twelve different solutions covering the range 0.0005 to 1.0 N were used. The cells, except No. III, were then given a much heavier platinization on top of the light platinization, as is shown in Table I. The electrodes at this stage did not have the deep sooty black color which can be obtained by using platinizing solutions containing a trace of lead acetate but were black with a slightly grayish or metallic appearance. Then the second series of measurements on cell resistance ratios was carried out.

The solutions used in the second series were approximately of the same concentration but not identical with the solutions used in the first series. The ratio of the specific conductance of these solutions can be computed from the data on cell III because in this case the cell itself was unchanged, but no direct comparison can be made between the first and second series without making due allowance for the difference in specific conductance, and for the fact that the cell constants may have been slightly changed by the additional platinization.

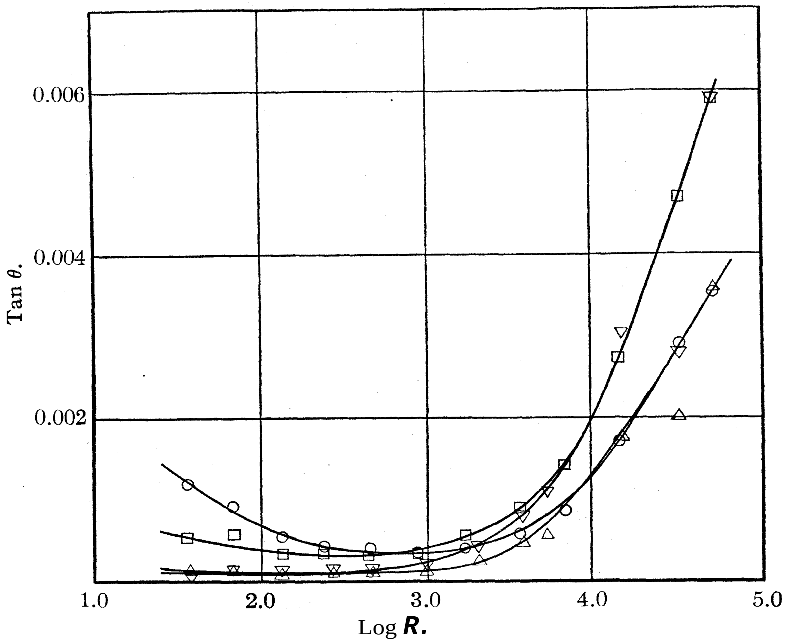

Fig. 2.—Cell I: ○, 1090 L; 0,2280 L; △, 1090 H; ▽, 2280 H.

The primary data of these cell comparisons are shown in Tables II to VI, inclusive, in which the successive columns have the significance: (1) the number of the solution of potassium chloride used; (2) the approximate concentration; **(3)** the resistance in ohms when measured with 1090 cycles, R'; (4) the capacitance in micromicrofarads required in parallel with the resistance box in the other arm of the bridge to give a balance, C_P, when using 1090 cycles; (5) the tangent of the phase angle, $\tan \theta = C_P\omega R$, when using 1090 cycles; (6) the resistance with 2280 cycles, R''; (7) the parallel capacitance at 2280 cycles; (8) the tangent of the phase angle at 2280 cycles; (9) the change in resistance caused by changing the frequency from 1090 to 2280 cycles, $-(R''-R')$, with sign reversed for convenience; (10) the percentage change in resistance with reversed sign, $-100(R'' - R')R'$.

The Significance of Phase Displacement in Cells.—Figures 2 to 6 give plots of tan θ against log R for each of the five cells at two frequencies and with two degrees of platinization. The log R is plotted as abscissa instead of R merely to avoid confusion due to crowding of the points at the lower resistances. In the legend under Figs. 2–10 the numbers 1090 and 2280 designate the frequency used, L signifies light platinization, and H heavy platinization.

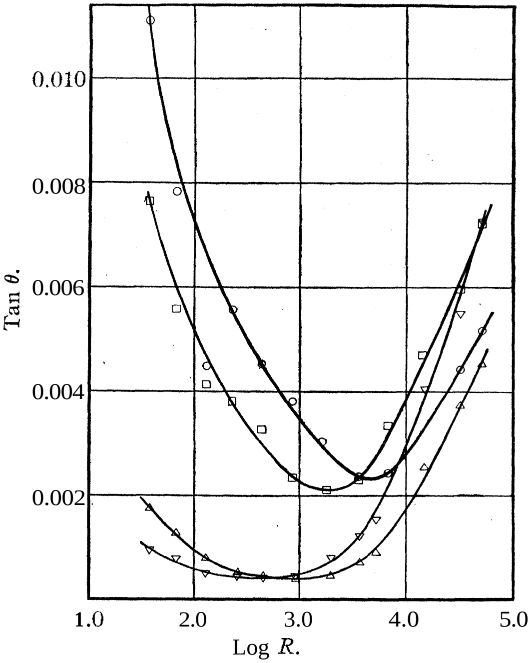

Fig. 3.—Cell II.

In these curves the outstanding feature is that the phase displacement goes through a minimum which indicates that there are two phenomena superimposed on each other. At low resistances the phase angle is undoubtedly one aspect of polarization. These data and curves make it evident that there is another and distinct disturbing effect which causes a phase displacement and which increases rapidly with the resistance being measured. This disturbance apparently also causes an error in the resistance which is responsible for the Parker Effect. Our task is, therefore, to analyze the data for the purpose of elucidating the nature of this disturbing effect and to ascertain the sign of the error in the resistance caused thereby and the factors controlling its magnitude and, if possible, to find a means of eliminating this error. From a study of these data and curves the following general conclusions may be drawn.

(1) The measured resistance with 2280 cycles, R", is always less than with 1090 cycles, R', when all other conditions remain unchanged. Tables II–VI give 109 instances of this without a single exception and this conclusion is in accord with much other experience in this Laboratory.

Table II

Cell Comparison Data. Cell I

Light Platinization

		f = 1090			f = 2280				
Soln.	Approx. concn.	R', ohms	C_P, μμf.	Tan θ $C_P\omega R$	R'', ohms	C_P μμf.	Tan θ $C_P\omega R$	$K'-R''$ ohms	$(R'-R'')/R$, %
1	0.0005	51,623.7	10	0.0035	51,512.0	8	0.0059	111.7	0.217
2	,0009	32,876.7	13	.0029	32,824.2	10	.0047	52.5	.160
3	.0019	14,717.7	17	.0017	14,704.7	13	.0027	13.0	.089
4	.0040	7,008.92	18	.00086	7,005.8	14	.0014	3.12	.045
5	.0077	3,677.98	23	.00058	3,677.23	17	.00090	0.75	.020
6	.016	1,675.4	35	.00040	1,675.13	23	.00055	.27	.016
7	.033	871.711	60	.00036	871.626	28	.00035	.085	.010
8	,065	447.96	130	.00040	447.913	50	.00032	.047	.010
9	.13	235.553	270	.00044	235.509	100	.00034	.044	.019
10	.25	133.295	600	.00055	133.276	180	,00034	.019	.014
11	.5	67.935	2000	.00093	67.916	590	.00057	.019	.028
12	1.0	36,380	4800	,00120	36.368	1050	.00055	.012	.033

Heavy Platinization

Soln.	Approx. concn.	R', ohms	C_P, μμf.	Tan θ $C_P\omega R$	R'', ohms	C_P μμf.	Tan θ $C_P\omega R$	$K'-R''$ ohms	$(R'-R'')/R$, %
21	0.0005	51,808.8	10	0.0035	51,675.3	8	0.0059	133.5	0.258
22	.0009	32,721.4	9	.0020	32,681.1	6	.0028	40.3	.123
23	,0020	15,161.1	17	.0018	15,148.4	14	.0030	12.7	.084
24	.005	5,456.20	15	.00056	5,454.47	14	.0011	1.73	.032
25	.008	3,836.87	18	.00047	3,836.14	15	.00082	0.73	.019
26	,013	2,046.77	18	,00025	2,046.61	15	.00044	.16	.008
27	.031	941.065	20	,00013	941.015	15	.00020	.050	.005
28	.065	470.156	33	.00011	470.14	23	.00015	.016	.003
29	.13	267.620	65	.00012	267.613	36	.00014	.007	.003
30	.25	132.529	83	.00007	13'2.523	88	.00009	.006	.005
31	.50	68.853	315	.00015	68.849	145	.00014	.004	,006
32	1.00	37.774	500	.00013	37.771	210	.00011	.003	.008

Table III

Cell Comparison Data. Cell II

Light Platinization

		f = 1090			f = 2280				
Soln.	Approx. concn.	R', ohms	C_P, μμf.	Tan θ	R'', ohms	C_P, μμf.	Tan θ	$R'-R''$, ohms	$(R'-R'')/R$, %
1	0.0005	50,411.4	15	0.0052	50,317.7	10	0.0072	93.7	0.185
2	.0009	32,109.7	20	,0044	32,059.4	13	.0060	50.3	.157
3	.0019	14,380.0	. .	. . . . .	14,361.6	23	.0047	18.4	.128
4	.0040	6,851.96	52	.0024	6,846.12	28	.0033	5.84	.085
5	.0077	3,597.36	95	.0023	3,594.87	45	.0023	2.49	.070
6	.016	1,640.08	270	.0030	1,638.60	90	.0021	1.48	.090
7	.033	854.19	650	.0038	853.14	190	.0023	1.05	.120
8	.065	439.536	1500	,0045	438.811	520	.0033	0.725	.165
9	.13	231.68	3500	.0055	230.987	1150	.0038	,693	.300
10	.25	131.180	5000	.0045	130.904	2200	.0041	.276	.211
11	.50	67.235	17000	.0078	67.000	5800	.0056	.235	.348
12	1.0	36.175	44800	.0111	36.025	14800	.0076	.150	.415

TABLE III (Concluded)

Heavy Platinization

		f = 1090			f = 2280				
Soln.	Approx. concn.	R', ohms	C_P, μμf.	Tan θ	R'', ohms	C_P, μμf.	Tan θ	$R'-R''$, ohms	$(R'-R'')/R$, %
21	0.0005	50,593.7	13	0.0045	50,497.7	10	0.0072	96.0	0.190
22	.0009	31,959.2	17	.0037	31,914.3	12	.0055	44.9	.141
23	.0020	14,814.7	25	.0025	14,795.2	19	.0040	19.5	.132
24	.005	5,332.59	25	.00091	5,330.39	20	.0015	2.20	.041
25	.008	3,749.84	28	.00072	3,748.91	23	.0012	0.93	.025
26	.013	2,000.48	33	.00045	2,000.26	28	.00080	.22	.011
27	.031	919.930	65	.00041	919.833	33	.00043	.10	.011
28	.065	459.691	140	.00044	459.646	65	.00043	.045	.045
29	.13	261.761	300	.00054	261.726	120	.00045	.035	.035
30	.25	129.698	890	.00079	129.678	280	.00052	.020	.020
31	.5	67.460	2750	.00127	67.448	810	.00078	.012	.012
32	1.0	37.080	6900	.00175	37.070	1800	.00096	.010	.010

TABLE IV

CELL COMPARISON DATA. CELL III

Heavy Platinization

		f = 1090			f = 2280				
Soln.	Approx. concn.	R', ohms	C_P, μμf.	Tan θ	R'', ohms	C_P, μμf.	Tan θ	$R'-R''$ ohms	$(R'-R'')/R$, %
1	0.0005	50,920.5	8	0.0028	50,888.5	8	0.0058	32.0	0.063
2	.0009	32,415.1	9	.0020	32,402.1	8	.0037	13.0	.040
3	.0019	14,502.1	14	.0014	14,499.6	11	.0023	2.5	.017
4	.0040	6,905.92	10	.00047	6,904.2	9	.00089	1.72	.025
5	.0077	3,623.70	12	.00030	3,623.24	10	.00052	0.46	.013
6	.016	1,650.54	18	.00020	1,650.46	13	.00031	.08	.005
7	.033	858.755	21	.00012	858.74	12	.00015	.015	.002
8	.065	441.218	45	.00014	441.205	20	.00013	.013	.003
9	.13	231.999	100	.00016	231.992	33	.00011	.007	.003
10	.25	131.296	260	.00024	131.288	70	.00013	.008	.006
11	.50	66.897	1000	.00046	66.893	230	.00022	.004	.006
12	1.00	35.824	2900	.00071	35.819	520	.00027	.005	.014

Heavy Platinization

21	0.0005	51,118.8	6	0.0021	51,081.8	6	0.0044	37.0	0.072
22	.0009	32,268.8	8	.0018	32,249.9	6	.0028	18.9	.059
23	.0020	14,942.8	14	.0014	14,936.5	12	.0026	6.3	.042
24	.005	5,376.34	10	.00037	5,375.56	9	.00069	0.78	.014
25	.008	3,780.46	13	.00034	3,780.11	11	.00060	.35	.009
26	.013	2,016.60	10	.00014	2,016.51	9	.00026	.09	.004
27	.031	927.141	14	.00009	927.111	9	.00012	.030	.003
28	.065	463.221	34	.00011	463.204	16	.000106	.017	.004
29	.13	263.665	75	.00013	263.657	29	.00011	.008	.003
30	.25	130.571	200	.00018	130.563	40	.000075	.008	.006
31	.50	67.834	700	.00032	67.828	170	.00016	.006	.009
32	1.0	37.217	1900	.00048	37.212	320	.00014	.005	.013

TABLE V

CELL COMPARISON DATA. CELL IV

Light Platinization

		f = 1090			f = 2280				
Soln.	Approx. concn.	R', ohms	C_P, $\mu\mu$f.	Tan θ	R'', ohms	C_P, $\mu\mu$f.	Tan θ	$R'-R''$, ohms	$(R'-R'')/R$, %
5	0.0077	43,101.1	23	0.0068	43,019.3	20	0.0123	81.8	0.190
6	.016	19,657.2	25	.0033	19,644.2	23	.0065	13.0	.066
7	.033	10,230.3	21	.0015	10,228.0	19	.0028	2.3	.023
8	.065	5,257.42	21	.00076	5,256.41	18	.0014	1 01	.019
9	.13	2,764.51	26	.00049	2,764.26	21	.0008	0 25	.009
10	.25	1,564.88	35	.00038	1,564.72	20	.00045	16	.010
11	.5	797.53	60	.00033	797.45	30	.00034	08	.010
12	1.0	427.183	130	.00038	427.159	60	.00037	024	.006
Heavy Platinization									
25	0.008	45,017.9	19	0.0059	44,959.5	18	0.0116	58.4	0.13
26	.013	24,025.0	20	.0033	24,013.0	18	.0062	12.0	.050
27	.031	11,046.2	21	.0016	11,044.9	21	.0033	1.3	.012
28	.065	5,519.75	15	.00057	5,519.50	15	.0012	0.25	.004
29	.13	3,142.14	17	.00037	3,142.04	15	.00067	.10	.003
30	.25	1,555.96	21	,00022	1,555.93	18	.000403	.03	.002
31	.50	808.498	20	.00011	808.480	14	.000106	.018	.002
32	1.00	443.632	40	,00012	143.625	21	.000103	.007	.002

(2) For any given cell and frequency the change in apparent resistance caused by a change in frequency, $-(R'' - R')$, increases in magnitude with the resistance being measured throughout the range from 19 to 51,000 ohms.

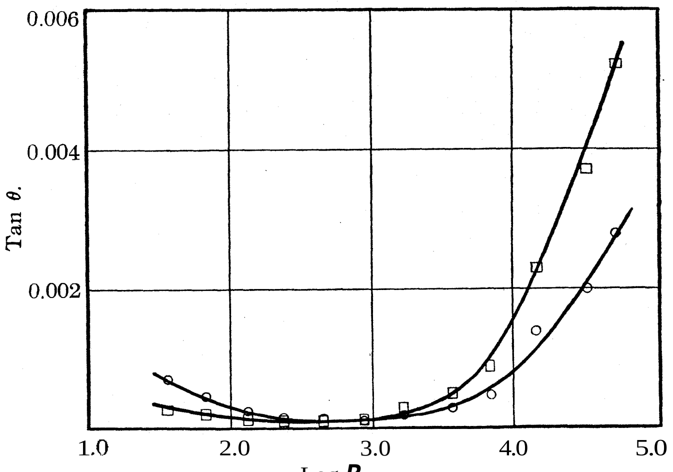

Fig. 4.—Cell III: O, 1090: □, 2280.

(3) For any given cell and frequency the numerical value of the percentage change in resistance caused by a change in frequency, $-100(R'' -$

TABLE VI

CELL COMPARISON DATA. CELL V

Light Platinization

		f = 1090			f = 2280				
Soln.	Approx. concn.	R', ohms	C_P, μμf.	Tan θ	R'', ohms	C_P, μμf.	Tan θ	$R'-R''$, ohms	$(R'-R'')/R$, %
1	0.0005	14,544.2	16	0.0017	14,541.5	16	0.0033	2.7	0.019
2	.0009	9,256.1	11	,00070	9,255.2	10	.0013	0.9	.010
3	.0019	4,139.3	23	.00065	4,138.88	11	.00065	.42	.010
4	.0040	1,970.OF	60	.00081	1,969.74	23	,00065	.32	.016
5	.0077	1,033.74	130	.00092	1,033.46	42	.00062	.28	.027
6	.016	.....	..	....	470.895	130	,00088	..	..
7	.033	245.249	1000	.0017	245.048	350	.0012	.201	.08
8	,065	126.09	2000	.0017	125.969	870	.0016	.121	.09
9	.13	66.349	4300	.0019	66.292	1850	.0018	,057	.09
10	.25	37.588	10000	.0026	37.551	4300	.0023	.037	.10
11	.5	19.160	26000	.0034	19.148	7000	.0019	.012	.06
				Heavy Platinization					
21	0.0005	14,595.2	12	0.0012	14,593.1	12	0.0025	2.1	0.014
22	.0009	9,206.04	8	.0005	9,205.5	8	.0011	0.54	.006
23	.0020	4,262.19	9	,00026	4,261.99	8	.00049	.20	.005
24	.005	1,533.04	19	.00020	1,532.95	13	.00028	.09	.006
25	.008	1,077.93	22	,00016	1,077.86	13	.00020	.07	.007
26	.013	575.117	43	.00017	575.08	22	.00018	.037	.006
27	.031	264.381	130	.00023	264.361	55	.00021	.020	.008
28	.065	132.095	320	.00029	132.090	100	.00019	,005	.004
29	.13	75.202	930	.00048	75.188	310	.00033	.014	.019
30	.25	37.241	2600	.00066	37.231	700	,00037	.010	.027
31	.50	19.352	6900	.00091	19.345	1750	,00048	.007	.036

$R')/R'$, goes through a minimum at intermediate values of the resistance. (This is not shown by Cell IV, for which data at very low resistances are not available.)

(4) For any given cell and frequency the phase displacement, $\theta = \tan^{-1}C_P\omega R$, goes through a minimum at intermediate values of the resistance being measured. This minimum is shown in nineteen cases in the tables. In the case of Cell IV at 2280 cycles when heavily platinized the minimum was not observed but it would probably be found below the lowest resistance measured.

(5) Increasing the frequency or increasing the platinization causes the minimum in the phase angle to occur at a lower resistance.

At low resistances, where polarization has the predominating influence, the following characteristics appear.

(6) For any given cell and frequency the parallel capacitance always has its greatest value at the lowest resistance measured, and decreases rapidly from this high value with increasing resistance.

(7) The parallel capacitance is much less at 2280 cycles than at 1090.

(8) For any given cell and frequency the phase angle is reduced by increasing the resistance being measured.

(9) The phase angle is reduced by increasing the frequency.

(10) The effect of increasing the platinization is to reduce greatly the parallel capacitance, the phase angle, and the change in resistance caused by a change in frequency. This drop in parallel capacitance is doubtless due to an increase in the series capacitance since the two are related by the equation

$$C_s = \frac{1}{C_P\omega^2 R^2} \qquad (4)$$

(11) A comparison of the curves for the different cells indicates that polarization and the related effects are reduced by increasing the area of the electrodes and increasing the distance between them.

At high resistances, where polarization becomes relatively insignificant and the disturbance responsible for the Parker Effect predominates, the phenomena are very different.

(12) The parallel capacitance becomes nearly independent of the resistance and of the frequency.

(13) The phase angle is increased by increasing the resistance or by increasing the frequency.

(14) The parallel capacitance and phase angle are not influenced by the degree of platinization.

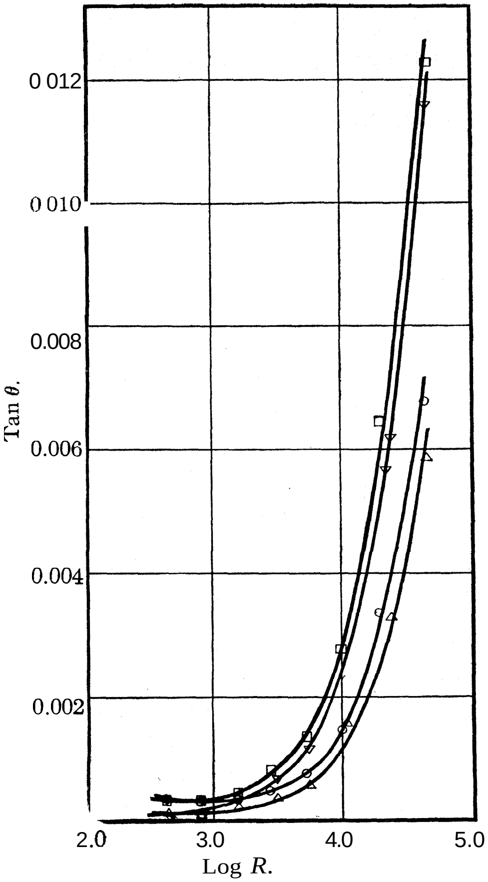

Fig. 5.—Cell IV: O, 1090 L; □, 2280 L; A, 1090 H; V, 2280 H.

The Cell Resistance Ratios—Polarization and Parker Effect.—From these data on five cells we can obtain ten intercomparisons similar to Parker's, each at two frequencies and with two degrees of platinization. All of the possible forty curves have been drawn but since they are not all mathematically independent, we have selected illustrative examples of the different types for reproduction in Figs. 7 to 10. The cell resistance ratios from which these curves are drawn are not printed, in order to save space, because they can be readily computed by anyone interested from the data in Tables II to VI.

The curves obtained are of varied types.[9] The curve depicting the ratio V/III shows a steep fall with increasing resistance at low resistance (especially when unplatinized) and a steep rise at high resistances, giving a sharp minimum. I/III, on the other hand, has a negative slope throughout—gentle at low resistances but steep at high resistances. II/III is like I/III in showing a negative slope throughout, but is much steeper at low resistances than at high resistances. Attention is called to the fact that in drawing curve II/III it was necessary to use a vertical scale only about $^1/_{20}$ of that used in the other cases. In the case of V/IV [not printed] when lightly platinized both frequencies give curves with a sharp minimum similar to V/III; when heavily platinized and using 1090 cycles there is a minimum although a flat one, but with 2280 cycles the minimum disappears entirely, giving a positive slope throughout.

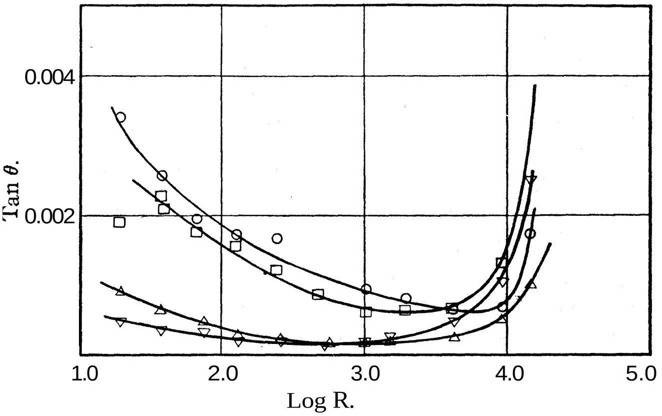

Fig. 6.—Cell V: O, 1090 L; □, 2280 L; A, 1090 H; V, 2280 H.

This variation in the shape of curves in different cases is clearly due to the fact that there are errors in both cells and the location of the points above or below the true cell constant ratio depends on the sign of the error and on which of the two cells has the greater fractional error. With only resistance ratio curves as a guide it would be extremely difficult to decide as to which of the two cells has the predominating influence and as to the sign of the error. Indeed, as will be shown, Parker himself reached

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[9] In comparing these curves with those of Parker it should be noted that we have plotted log R as abscissa instead of R, to avoid undue crowding of points at low resistances. It should also be noted that Parker always puts the cell of lowest cell constant in the numerator, whereas we have found it desirable in all cases in which cell III was used to put this cell in the denominator to facilitate comparison of the different curves.

an erroneous conclusion on these questions at resistances high enough so that polarization ceases to be the controlling influence; but by using our tan θ curves as an indication of the quality of the cells, together with a consideration of the influence of the frequency and of the degree of platinization, we hoped to be able to unravel the nature of the disturbances and to determine the sign and perhaps the magnitude of the errors.

These data confirm Parker's results in showing that the ratio of the resistances of two cells when filled with a common solution is not independent of the concentration of the solution used. An extreme example is given by a comparison of cells V and II when both were lightly platinized. When using 1090 cycles and with both cells filled with a normal potassium chloride solution, the ratio of the resistances was 0.28497, whereas when both were filled with a 0.0005 N solution the ratio was 0.28851, a difference of 1.25%.

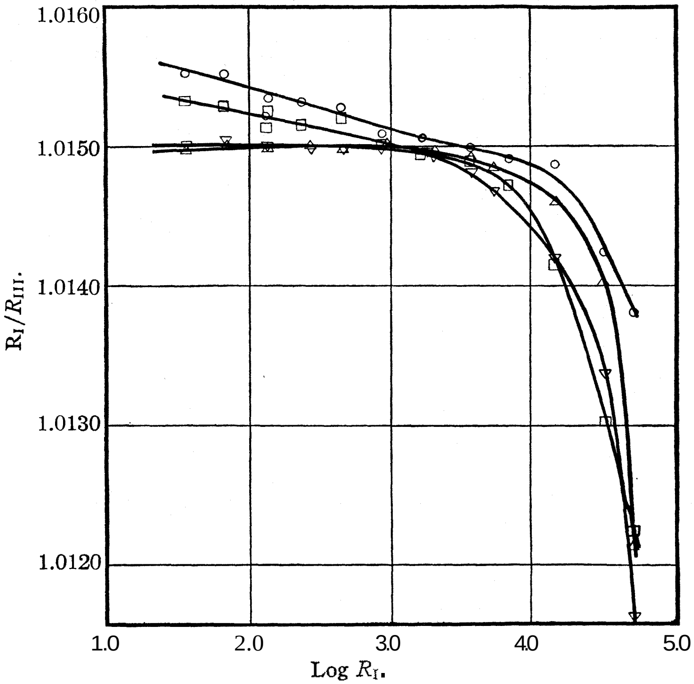

Fig. 7.—Cell resistance ratios, I/III: O, 1090 L; □, 2280 L; A, 1090 H; ▽, 2280 H.

Although our various curves differ among themselves greatly in slope and curvature, none of them shows both a maximum and a minimum, as do some of Parker's. His curves indicate clearly that in some of his experiments there were at least three disturbances present, but ours show indications of only two causes of error. It seems probable that this simplification of the problem has been accomplished by the improvements in our bridge as compared to that used by Parker. These improvements have been described in the first and second papers of this series. Of the two disturbances which remain, the one which predominates at low resistances is clearly polarization and the other is presumably responsible for the Parker Effect.

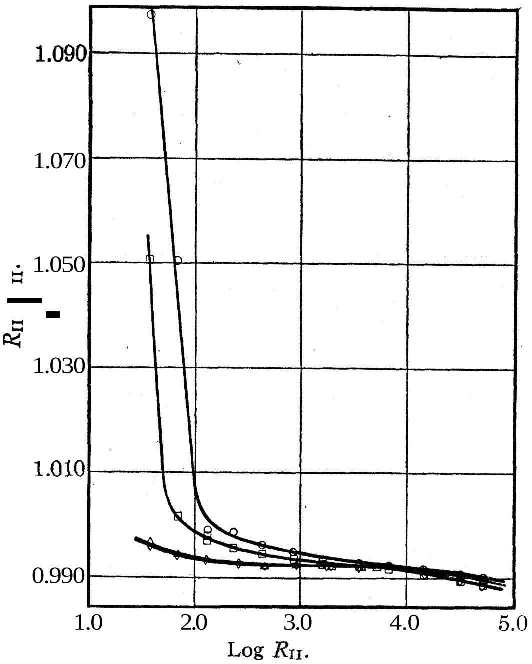

Fig. 8.—Cell resistance ratios, II/III: ○, 1090 L; □, 2280 L; A, 1090 H; V, 2280 H.

Polarization has long been known and has been the subject of many investigations. One of the effects of polarization is to cause a capacitance in series with the resistance of the cell, as is clearly shown by the phase displacement. If this were a pure capacitance and followed the harmonic laws characteristic of geometric capacitance, it could be compensated without causing an error in the resistance measurements. But it has been demonstrated by Wien,[10] Miller,[11] and others that one aspect of polarization is an added polarization resistance in series with the true electrolytic resistance of the solution in the cell. The error in the measured resistance of a cell due to polarization is always positive. The polarization resistance is independent of the distance between the electrodes and therefore the percentage error caused by polarization resistance can be decreased by using cells of high cell constant. Of two cells which are alike except in the distance between the electrodes, the shorter cell will have the relatively greater polarization error when both are filled with the same solution. Polarization can also be minimized, as was suggested long ago by Kohlrausch, by platinization of the electrodes, by the use of high frequencies and by the use of large electrodes. The behavior of our cells at the lower resistances as shown in the tables and curves and

[10] M. Wien, *Wied. Ann.*, 58, 37 (1896).

[11] C. Miller, Phys. Rev., [2] 22, 622 (1923).

summarized above (see pp. 424–425, paragraphs numbered 6–11) is clearly consistent with this interpretation. Increasing the platinization or increasing the frequency at low resistances always causes a decrease in the phase angle and tends to make the cell resistance ratios more nearly constant. From the consideration of the dimensions of our cells we should expect that the influence of polarization would be the greatest in cell II and decrease in the order V, III, I, IV. It will be apparent from these curves, data and discussion that in order to minimize errors due to polarization it is desirable to use a high frequency and to use a cell of high cell constant so that the resistance being measured will be high; but both of the expedients aggravate the disturbance responsible for the Parker Effect and, therefore, do not furnish a satisfactory solution of the problem unless and until the cause of the Parker Effect can be ascertained and a remedy for it invented.

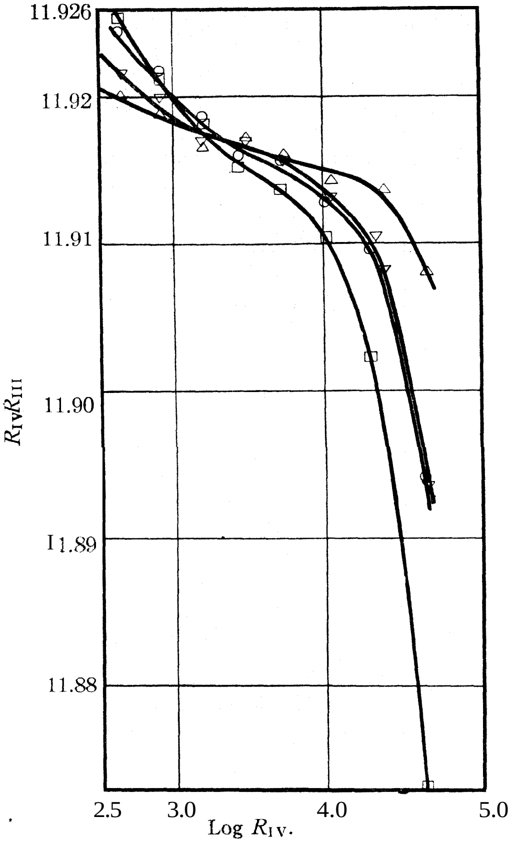

Fig. 9.—Cell resistance ratios, IV/III: ○, 1090 L; □, 2280 L; A, 1090 H; ▽, 2280 H.

The disturbance which predominates at the higher resistances and is presumably responsible for the Parker Effect is clearly different from polarization. It is independent of the degree of platinization and is aggravated rather than cured by an increase of frequency. The hypothesis that adsorption is responsible, as suggested by Parker[12] and supported by Randall and Scott,[13] is discredited by the fact that the effect was not increased by a tenfold increase in the amount of spongy platinum present. This disturbance is like polarization in causing the current to lead the voltage but it differs in that the phase displacement increases rapidly with increased resistance being measured, whereas the

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[12] H. C. Parker, THIS JOURNAL, 45, 1378 (1923); 45, 2021 (1923).

[13] M. Randall and G. N. Scott, ibid., 49, 642 (1927).

phase displacement due to polarization decreases with the resistance, as is shown by the occurrence of a minimum in the phase displacement and the rapid rise at the higher resistances. It also differs from polarization in that the phase displacement corresponds to a parallel capacitance which is independent of the frequency and the resistance. This suggests that we are dealing with a real parallel capacitance instead of a series capacitance.

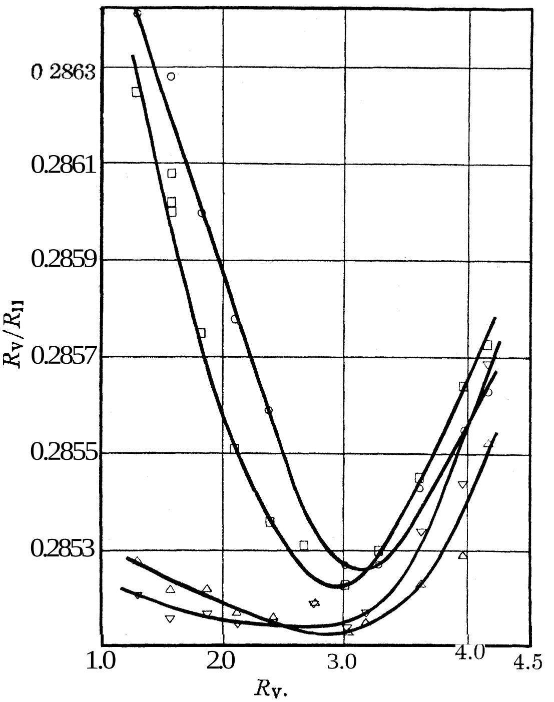

Fig. 10.—Cell resistance ratios, V/III: O, 1090 L; □, 2280 L; A, 1090 H; ▽, 2280 H.

We now come to the question of the sign of the error in the resistance which is responsible for the Parker Effect. Parker accounted for the positive slope in his resistance ratio curves in the following manner. ‘‘It is evident from the direction of the effect in the more dilute solutions that if the correction which should be applied to the resistances to give a constant ratio, is *relatively* greater for the shorter cell, then the correction is negative." . . "The facts gathered thus far indicate that the effect is in the cell itself and that the correction is negative, that is, that the resistances, R, should be corrected by an amount ΔR, which should be subtracted from the apparent resistance.’’[14] But our cells show both positive and negative slopes in the resistance ratio curves at the higher resistances. The rapid increase in the phase displacement at the higher resistances and the increased slope of the resistance ratio curves at the high resistances are clearly related. Both the phase displacement and the slope of the resistance ratio curves are increased by increasing the frequency, thus clearly showing that the disturbance responsible for the Parker Effect is increased by increasing the frequency. But since increasing the frequency always decreases the apparent resistance at high resistance as well as at low resistances, it follows that the error in the resistance due to the Parker Effect must always be negative and increase in magnitude with the frequency and

[14] H. C. Parker, THIS JOURNAL, 45, 1375 (1923).

the resistance being measured. Hence, contrary to Parker's conclusion, the correction must be positive. The fact that the error is always negative suggests a shunt path for the current which is electrically in parallel with the solution between the electrodes. A shunt is much more effective across a high resistance than across a low resistance, which is the case for the disturbance responsible for the Parker Effect. The clear indication of a parallel capacitance given by a study of the data suggests that the shunt is not a pure resistance but contains the equivalent of a condenser, The influence of a shunted condenser would increase with the frequency, which accords with our experience. But if the impedance in the shunt were due solely to capacitative reactance, it could be fully compensated by a condenser shunted across the resistance box without causing an error in the resistance, which is not the case. We must, therefore, infer that the shunt contains resistance as well as reactance. And now a renewed inspection of the pipet cells with the vision thus sharpened reveals the shunt clearly; it consists of the resistance in the filling tube, and the capacitance through the glass walls of the cell and the thermostat oil between the solution in the filling tube and the mercury in the contact tube of opposite polarity; together with distributed capacitance between the electrolyte in the cell proper and the filling tubes and contact tubes, as shown diagrammatically in Fig. 11. Having once seen the shunt we wonder why no one ever saw it before, and are chagrined that our eyes had been blind so long.

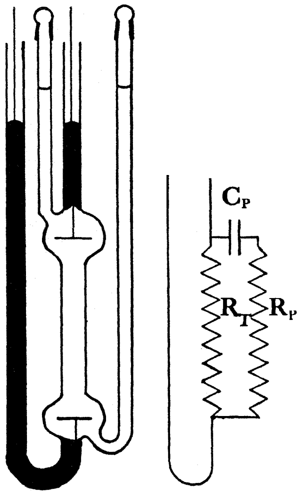

Fig. 11 —Capacitance bypaths in pipet cell.

Since according to this hypothesis the disturbance causing the Parker Effect is not primarily an electrode effect, it would be expected that the degree of platinization will have little if any influence, which is in accord with our experience.

The earlier investigators who came the nearest to the solution of this problem appear to be Morgan and Lammert.[15] They measured the resistance of a series of solutions covering a wide range of resistance at two different frequencies in several cells with unplatinized electrodes. They have observed points (1), (2). and (3) listed above (pp. 420–423). They say: "Throughout the work the capacities were measured and found to be

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[15] J. L. R. Morgan and O. M. Lammert, THIS JOURNAL, 45, 1693–1697 (1923). This paper was published only one month after the first paper of Parker [*ibid.*, 45, 1366 (1923)] and therefore Morgan and Lammert must have written their manuscript before they had an opportunity to read Parker's paper.

greater at 500 cycles than at 1000 cycles, but as the difference in the resistance at the two cycles [sic] increased, the difference in the capacities decreased. Inasmuch as the condensers were of the type used to balance out capacity in the cell and were not standardized, the actual values are qualitative and are not given." They evidently anticipated our point (7) above without publishing the proof; but they did not interpret the capacitance readings either in terms of phase displacement in the cells or as an indication of a capacitative shunt which could cause an error in the resistance which is a function of the frequency, nor did they distinguish between errors in resistance due to polarization and errors due to capacitative shunt or offer any interpretation of or cure for the Parker Effect.

Mathematical Analysis of Errors Due to Shunt.—In the pipet cells as usually designed the electrodes are placed horizontally one above the other and the electrical contact to the electrodes is made by means of wires dipping into the glass tubes which are commonly filled with mercury to the level of the liquid in the thermostat. These contact tubes and the filling tubes through which the electrolyte is added to the cell are commonly brought out of the thermostat vertically and in close proximity to each other, thus creating capacitance between them as indicated diagrammatically by C_P in Fig. 11. This arrangement provides an additional path for the current through the resistance of the electrolyte in the filling tube, R_P, and the capacitance between the filling tubes and the contact tubes, C_P. If the thermostat is filled with water instead of oil the resistance in the thermostat liquid will be part of the shunt resistance, but since it is known that the use of water introduces errors, this case will not be considered further here. In an oil-filled thermostat the glass parts of the cell with the intervening oil may be regarded as a pure capacitance, and all of the shunt resistance is in the filling tubes and contact tubes. This shunt across the cell obviously tends to make the apparent resistance of the cell less than the true resistance of the electrolyte between the electrodes. The capacitance in the shunt is of course distributed along the resistance and therefore a precise analysis of the problem in the case of any given cell would require a precise knowledge of the geometrical form, the dielectric constant, and power factor of the glass used and of the thermostat liquid; and, even with all of these data at hand, would be a mathematical problem of great complexity.[16] For the sake of analyzing the effects of this shunt we can assume that a shunt composed of a resistance, R_P, and a capacitance, C_P, in series across the electrodes is electrically equivalent to the distributed capacitance and resistance actually present, and that dielectric

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[16] *See* Shedlovsky, THIS JOURNAL, 52, 1793 (1930), for an interesting attempt to solve a similar problem for a simpler case in which the capacitance is assumed to be uniformly distributed along the resistance.

losses in glass and oil are negligible in comparison with the losses in the filling tube The reactance of the shunt is

$$X_P = \frac{1}{\omega C_P} = \frac{1}{2\pi f C_P} \tag{5}$$

and the impedance of the shunt is

$$Z_P = R_P + jX_P \tag{6}$$

Let R_T be the true resistance of the cell;[17] R be the measured resistance of the combination of cell and shunt at the frequency of f; X, the measured reactance of the combination at frequency f; $Z = R + jX$, the impedance of the combination at frequency f. Then by the law of parallel branches

$$\frac{1}{Z} = \frac{1}{R_T} + \frac{1}{R_P + jX_P} = \frac{R_T + R_P + jX_P}{R_T(R_P + jX_P)} \tag{7}$$

$$Z = \frac{R_T(R_P + jX_P)}{R_T + R_P + jX_P} = \frac{R_T(R_P + jX_P)}{(R_T + R_P + jX_P)} \times \frac{R_T + R_P - jX_P}{R_T + R_P - jX_P} \tag{8}$$

$$Z = \frac{R_T^2 R_P + R_T R_P^2 + R_T X_P^2}{(R_T + R_P)^2 + X_P^2} + \frac{jX_P R_T^2}{(R_T + R_P)^2 + X_P^2} \tag{9}$$

Therefore $$R = R_T \frac{(R_T R_P + R_P^2 + X_P^2)}{(R_T + R_P)^2 + X_P^2} = R_T \left(1 - \frac{R_T R_P + R_T^2}{(R_T + R_P)^2 + X_P^2}\right) \tag{10}$$

and $$X = X_P \frac{R_T^2}{(R_T + R_P)^2 + X_P^2} \tag{11}$$

Let ΔR designate the error due to the shunt, then

$$R = R_T + AR \tag{12}$$

and hence the error

$$\Delta R = -\frac{R_T(R_T R_P + R_T^2)}{(R_T + R_P)^2 + X_P^2} \tag{13}$$

or the fractional error

$$\frac{AR}{R_T} = -\frac{R_T R_P + R_T^2}{(R_T + R_P)^2 + X_P^2} \tag{14}$$

Since none of the terms in this equation can ever have a negative real value, the error is always negative. But

$$X_P = \frac{1}{\omega C_P} \tag{5}$$

$$\frac{\Delta R}{R_T} = -\frac{(R_T R_P + R_T^2)\omega^2 C_P^2}{(R_T + R_P)^2 \omega^2 C_P^2 + 1} \tag{15}$$

When working under such conditions that polarization is negligible, unless the cell is of poor design, C_P will be about 20 $\mu\mu$f. or less. If C_P has this

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[17] It will be noted that in this mathematical analysis of the effect of the shunt, the cell proper (the electrodes and the electrolyte between them) is treated as a pure resistance. This is strictly true only if the reactance of the cell $X_C = 0$, that is, if the reactance due to polarization is negligible. An inspection of Curves 2–6 indicates clearly that for well-platinized electrodes the phase angle and hence the reactance falls rapidly with increasing resistance and would become negligible above 1000 ohms if the Parker Effect were not present.

value, 2×10^{-11} farads, and the measurement is made with 5000 cycles ($\omega = 31{,}400$; $\omega^2 = 10^9$) or less, and if the total resistance of $R_T + R_P$ does not exceed 100,000 ohms, the value of $(R_T + R_P)^2\omega^2C_P^2$ will not be greater than $10^{10} \times 10^9 \times 4 \times 10^{-22} = 4 \times 10^{-3}$. Under these circumstances if we ignore this term in the denominator of Equation 16, the error in $\Delta R/R$ will not be greater than 0.4%. With a frequency of 1000 (which is that most commonly used) and $C_P = 20$ $\mu\mu$f. and $R_T + R_P = 100{,}000$, the error in $\Delta R/R$ due to using the simpler form cannot exceed 0.02%. Therefore, at audio frequencies, except in the case of cells of abnormally bad design, $(R_T + R_P)^2\omega^2C_P^2$ will be small in comparison with 1 and therefore it will be approximately true that

$$\Delta R/R_T = -(R_TR_P + R_T^2)\omega^2C_P^2 \tag{16}$$

A further simplification is possible for the case of measurements made with an equal arm bridge which has been designed so that the capacitances between the arms are small and properly balanced by the earthing device, which is the case in our bridge, and if the conditions are such that polarization is negligible. In such a case the condenser shunted across the resistance box when adjusted so as to give a phase angle equal to that of the cell will have a capacitance, C_R, very nearly equal to the capacitance in the shunt across the cell, and the fractional error due to this capacitance[18] on the resistance box will be $-R_R^2\omega^2C_R^2$ which will be substantially equal to the $-R_T^2\omega^2C_P^2$ and thus will compensate for one term in the equation for the error in the cell, leaving as the net fractional error due to capacitance and resistance in the shunt across the cell approximately

$$\Delta R/R_T = -R_TR_P\omega^2C_P^2 \tag{17}$$

The actual error is therefore approximately

$$\Delta R = -R_PR_T^2\omega^2C_P^2 = -R_P \tan^2\theta \tag{18}$$

Combining Equations 18 and 12 gives

$$R = R_T - R_PR_T^2\omega^2C_P^2 = R_T - R_P \tan^2\theta \tag{19}$$

Experimental Verification of the Shunt Theory.—For any given cell filled with a given solution, R_T and R_P are constants, and ω can be held constant during a series of measurements. If now we vary C_P it may be predicted from Equation 19 that an increase in C_P will result in a decrease in the measured resistance, R, which will be proportional to the square of the total capacitance in the shunt. In order to make this test the capacitance in the shunt was artificially increased by connecting one lead wire from a variable air condenser to the mercury in one of the contact tubes, and connecting the other lead wire to a small piece of platinum foil dipping into the filling tube of opposite polarity. The total capacitance in the shunt due to the cell itself and to the condenser was then measured as usual by the capacitance required in parallel with the resistance in the

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[18] See Grinnell Jones and R. C. Josephs, THIS JOURNAL, 50, 1076 (1928).

other arm of the bridge. Resistance measurements were made with 500 and 2280 cycles at various settings from 0 to 25 $\mu\mu$f. of the variable air condenser which was in parallel with the cell.

The actual data are omitted for the sake of abbreviation and because the actual values are dependent on the particular cell and solution used. The variation of the apparent resistance with the capacitance, which alone is important for our present purposes, is shown in Fig. 12, in which we have plotted the measured resistance as ordinate against the square of the capacitance as abscissa. It will be observed that the experimental points at each frequency are on a straight line within the limit of error of the data. The intercept of each of these lines on the resistance axis should be the true resistance. It will be observed that the intercepts of the lines for the two frequencies are the same.

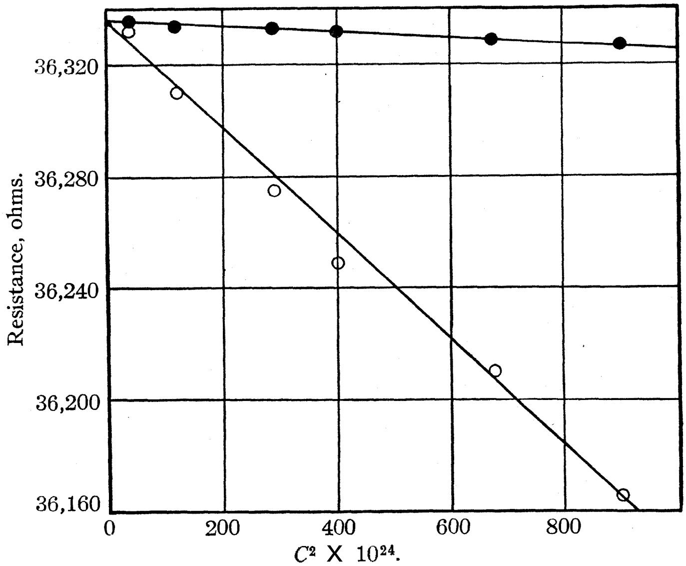

Fig. 12.—For upper curve $f = 500$; for lower curve $f = 2280$.

We next made a series of measurements in which the frequency was varied while the other factors were kept constant. In order to magnify the capacitance effect, 25 $\mu\mu$f. was added across the cell in the manner just described and the resistance determined at ten different frequencies within the range from 500 to 2280 cycles. In addition, the resistance was determined at several lower values of the capacitance at three frequencies. The actual results are omitted for the reasons explained above but they are shown in Fig. **13,** in which the measured resistance is plotted against the square of the frequency. As will be seen, the results at each frequency are on a straight line and these lines all have a common intercept on the axis of zero frequency which should be the true resistance. The value for the true resistance thus obtained is the same as that shown in the previous plot.

A special experiment was carried out to determine whether or not a significant change in capacitance and in resistance could be produced merely by a change in the relative position of the filling tube and the cell without any change in the electrodes or in the cell proper. A cell of the pipet type similar in shape to that shown in Fig. 11 was filled with potassium chloride solution and its resistance determined at several frequencies. The capacitance was 6 micromicrofarads. The filling tube was then extended and bent so as to conform with the shape of the cell and fitted closely to the cell. The effect was an increase in parallel capacitance to 14 micromicrofarads and a great increase in the variability of the resistance readings with change in frequency as shown in Table VII.

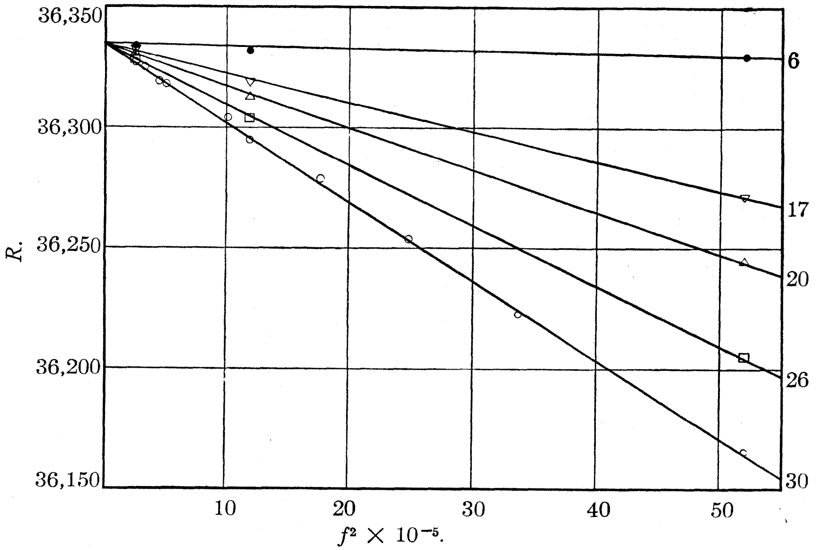

Fig. 13.—The values of C_P for these curves are given on the right-hand margin.

TABLE VII

CHANGE IN RESISTANCE CAUSED BY ALTERATIONS IN FILLING TUBE

Frequency. cycles	(Frequency)^2	Original filling tube $C_P = 6\mu\mu f$. Resistance ohms	New filling tube $C_P = 14\mu\mu f$. Resistance ohms
500	2.50×10^5	36,308	36,306
710	5.05		36,303
1090	11.9	36,306	36,295
1575	24.8		36,285
2280	52.0	36,304	36,258

The resistance readings when plotted against the square of the frequency give a straight line similar to that shown in Fig. **13.** This experiment definitely proves that altering the relative position of filling tubes and cell influences the parallel capacitance and that the resistance changes caused thereby vary with the frequency in accordance with our theoretical equation.

We next consider the effect of varying R_P while keeping the other factors constant. For this purpose we must use Equation 15 instead of the simplified form (17) because we wish to consider the influence of values of R_P greater than the upper limit assumed in deriving the simplified form. By differentiating Equation 15 with respect to R_P and holding all other factors constant and placing $\partial(\Delta R/R_T)/\partial R_P = 0$, it is possible to show that $\Delta R/R_T$ rises with increasing R_P to a maximum when $R_P = 1/C_P\omega$ and then falls again. The value of R_P which produces the maximum error is very large. Thus, for example, if $C_P = 10^{-11}$ farads, and $f = 2280$, $R_P = 1/(2 \times 3.14 \times 2280 \times 10^{-11}) = 7{,}000{,}000$ ohms. R_P will be far below this value in pipet cells of the usual design and the partial derivative indicated above will be positive. It will, therefore, be advantageous to design the cell so as to keep R_P low, provided this can be accomplished without increasing C_P.

In order to vary R_P while keeping all other factors constant, we devised a suitable expedient. A pipet type of cell was filled with a solution giving a resistance of about 50,000 ohms with both filling tubes filled as usual. Measurements were made at 500, 1090 and 2280 cycles and the true resistance ascertained by the method indicated in Fig. 13, and thus the error at 2280 cycles due to the shunt was estimated to be 0.02%. Then one of the filling tubes was emptied, leaving the inner wall wet with the solution, thus enormously increasing the resistance in the shunt without altering anything else. The error at 2280 cycles, estimated in the same manner, was now 0.10%. The inner wall of the filling tube was then dried by inserting a capillary tube and applying suction so that a stream of air passed down through the filling tube until it appeared to be dry. The error at 2280 cycles as determined in the same manner was now reduced to 0.025%. Apparently in this case the resistance in the filling tube was in excess of that which gave the maximum error. Although, owing to a lack of knowledge of the value of the resistance in the filling tube, the evidence of these experiments in support of our equation is not of the same quantitative nature as was obtained by varying the frequency and the capacitance, these experiments do support in a qualitative manner the predictions of our mathematical analysis.

Parker reported a difference in his cell constant ratios when the tube connecting his two cells was filled with the solution and when the solution in the tube was interrupted by an air bubble but could offer no explanation of this fact or reconcile it with his hypothesis that the error was due to adsorption. Our experiment just cited indicates that the reason for the influence of the bubble in the connecting tube was that the resistance in the shunt was changed thereby.

An interesting and important corollary of the analysis of the influence of the magnitude of the resistance in the shunt is that capacitance between the two lead wires and the mercury in the contact tubes in the pipet form of cell can do no harm provided an oil thermostat is used, because it is in effect a pure capacitance and can be compensated by a pure capacitance across the box without error in the resistance. In this case the resistance in the mercury and in the copper wires is negligible and the resistance in the oil enormously greater than the value $R_P = 1/C_P\omega$ which gives the maximum error. On the other hand, if water is used as the thermostat liquid, this water forms a part of a shunt between the contact tubes and may have a resistance which will cause a substantial error.

Parker Effect Due to Capacitative Shunt.—The expression for the error due to a capacitative shunt also accounts for the Parker Effect. If we use subscripts A and B to designate two different cells, in which the subscript A refers to the cell of lower cell constant, then the ratio of the measured resistance will be

$$\frac{R_A}{R_B} = \frac{R_{TA} + \Delta R_A}{R_{TB} + \Delta R_B} \tag{20}$$

Since AR is very small in comparison with R_T this can be developed into a power series and the higher terms neglected, giving

$$\frac{R_A}{R_B} = \frac{R_{TA}}{R_{TB}}\left(1 + \frac{\Delta R_A}{R_{BA}} - \frac{\Delta R_B}{R_B} + \dots\right) \tag{21}$$

Then by Equation 17

$$\frac{R_A}{R_B} = \frac{R_{TA}}{R_{TB}}\,[1 - (R_PR_T\omega^2C_P^2)_A + (R_PR_T\omega^2C_P^2)_B + \dots] \tag{22}$$

For any given cell, R_P will be proportional to R_T, since both are proportional to the specific resistance of the solution used, so that we may write $R_P = kR_T$, where the value of k will depend on the dimensions of the cell and of the filling tube and

$$R_T = (l/a)\ (1/\kappa)$$

and hence

$$\frac{R_A}{R_B} = \frac{R_{TA}}{R_{TB}}\left[1 - \left\{\left(\frac{kl^2}{a^2}\,C_P^2\right)_A - \left(\frac{kl^2}{a^2}\,C_P^2\right)_B\right\}\frac{\omega^2}{(\kappa)^2}\right] \tag{23}$$

It is thus evident that the variation of the resistance ratios R_A/R_B with increase in the specific resistance (or decrease in κ) will be positive if $(kl^2/a^2C_P^2)_B > (kl^2/a^2C_P^2)_A$ and negative in the converse case.

Our data, depicted in part in Curves 7 to 10, give examples of both positive and negative slope of the resistance ratio curves, and we have been able to correlate at least qualitatively the slope of these curves with the dimensions of the cells, which determine k, l/a and C_P, but the detail of this correlation must be omitted to save space. It may also be predicted from this equation that the slope of the resistance ratio curves (in the region where polarization is avoided), regardless of its sign will increase in magnitude with an increase in frequency and with an increase in the specific resistance of the solution used, which is fully in accord with our experience, and for a given pair of cells the slope can never change in sign with variation in frequency or variation in the specific conductance of the solution used, which is in accord with our experience.

Since sealing the cells together, as was done by Parker and in our experiments described above, would probably increase the capacitance,[19] it is to be expected that the error would be increased thereby, and it therefore seemed worth while to determine whether or not the effect is present in disconnected cells of the pipet type.

We therefore made another series of cell comparisons similar to those recorded above, using four separate disconnected cells of the pipet type, all heavily platinized, using 500, 1090 and 2280 cycles. The results are not published in detail, because they are similar in all respects to those given in Curves 7 to 10, except that the slopes are more gentle. The maximum variation in the resistance ratios observed in these experiments was only 0.05%, but the deviations are systematic and show in milder form the characteristics already observed with the connected cells.

This demonstration that Parker's expedient of sealing his two cells together to facilitate filling them with a common solution aggravates the error is important because it increases the reliance which may be placed on the great mass of data in the literature which were usually obtained with single cells.

Cell Design to Avoid Errors Due to Polarization and Shunt.—The theory of errors due to capacitative shunt has not only given a complete explanation of the nature and cause of the Parker Effect but has guided us in the design[20] of cells in which the error is eliminated. From the equation for the error due to a capacitative shunt, $\Delta R = -R_P R_T^2 \omega^2 C_P^2 = -R_P \tan^2 \theta$, it is evident that it will be well to beep each of the factors in this equation as low as other considerations permit.

It would of course be possible to design a cell without filling tubes as an integral permanent part of the cell but the filling tubes serve a useful purpose in facilitating the filling of the cells without contamination or evaporation of the solutions and should not be sacrificed except as a last resort. The resistance in the filling tubes might be reduced by making them of large diameter, but this tends to increase the capacitance, which

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[19] There is a certain analogy between capacitance shunt errors in cells which are sealed together and the effect of appended coils in a resistance box. See Grinnell Jones and R. C. Josephs, THIS JOURNAL, 50, 1084 (1928).

[20] See E. W. Washburn [THIS JOURNAL, 38, 2431 (1916)] for a mathematical analysis of cell design including a discussion of several considerations not taken up in detail in this paper.

offsets the gain. The filling tube should, however, be kept full of solution to avoid the high resistance of the surface film wetting the inner wall. The resistance in the filling tube will of course be proportional to the specific resistance of the solution being measured, and therefore this factor helps to set an upper limit to the resistance which can be measured accurately in any given cell.

It should be pointed out that although dipping electrode cells as commonly designed have no filling tube at all, nevertheless they do have a capacitative shunt. As usually designed, the electrodes are supported by two vertical contact tubes which are commonly close together. These electrodes should be immersed to a considerable depth in order that the lines of flow of the current may not be cut off by the surface of the solution and thus make the effective cell constant too greatly dependent on the depth of immersion of the electrodes. This creates a shunt across the path between the electrodes, through the glass walls of the contact tubes acting as a condenser and the resistance of the solution between these tubes. The impedance of this shunt will be a function of the frequency and errors due to capacitative shunt may therefore be expected with dipping cells, in spite of the fact that they have no filling tubes, especially when used with dilute solutions.

For any given solution the working value of the resistance will depend on the cell constant of the cell used, and can therefore be controlled within wide limits provided a sufficient number and variety of cells are available. But there is a limit below which it is not safe to go with R_T because of errors due to polarization. The limit will of course depend on the precision desired, on the frequency used, and on the dimensions and platinization of the electrodes. As the result of our experience we have set the lower limit of the resistance to be measured at about 1000 ohms when using well-platinized cells (see Figs. 2–6). But unless the upper limit can be many times the lower limit, a very great number of cells of closely graded cell constants will be needed to cover the whole range of specific conductance from that of very good conductivity water, 1×10^{-7}, up to about 0.5 for the best conducting aqueous solutions at room temperatures. Washburn[21] recommends that the upper limit be placed at 10,000 ohms, which with a lower limit of 1000 ohms would require seven cells to cover the entire range. To cover this range with four cells will require that the upper limit be placed at nearly 50,000 ohms, which is the upper limit which we have thought it desirable to strive for. It is, therefore, apparent that there are serious practical difficulties in any attempt to solve the problem by restricting the measurements to low values of the resistance to be measured.

An attempt to solve the problem by lowering the frequency would be

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[21] E. W. Washburn, THIS JOURNAL, **38**, 2450 (1916).

defeated by the fact that errors due to polarization increase rapidly with decrease in the frequency. Lowering the frequency tends to raise the safe lower limit of the resistance which can be measured without the appearance of an error due to polarization, which would defeat any attempt to make a substantial reduction in the shunt error by any considerable reduction of the frequency below 1000 cycles. Moreover, in the practical routine of conductance measurements it is possible with a suitable oscillator to change the frequency instantly by a mere turn of a dial and repeat the measurement at another frequency in a moment. If the measured resistance proves to be substantially independent of the frequency it shows that many of the possible errors, including polarization, shunt errors, and errors due to capacitance and inductance in the bridge and resistance boxes which have been discussed in the first paper of this series, have been eliminated. On the other hand, if there is a significant variation in the apparent resistance with variation in frequency it proves that some error is present and gives a clue as to the magnitude and nature of the error. Therefore, if it is possible to do so there will be a great advantage in avoiding the error due to a shunt by some other means than lowering the frequency, and judging of the success or failure of the attempt by noting the effect of variations in frequency.

The capacitance in the shunt can be reduced to a very small value by designing the cell so as to avoid close proximity of the filling tubes and the portions of the cell of opposite polarity. Each of the filling tubes should be placed at a safe distance from the other filling tubes and from the contact tube at the other end of the cell. This is most conveniently done by making the cells of the form shown in Fig. 14. Our experience indicates that a separation of 15 cm. between parts of the cell of opposite polarity is adequate. Shields placed close to any part of the cell should be avoided.

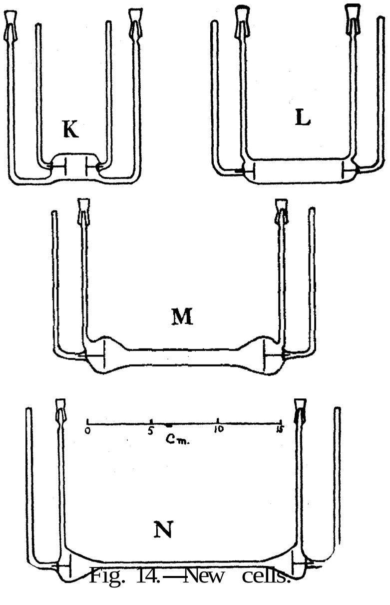

Fig. 14.—New cells.

New Cells—Description and Tests.—Four cells of the new form, designated K, L, M, N, which are depicted in Fig. 14 and whose dimensions are shown in Table VIII, were constructed and thoroughly tested.

These new cells were at first given a light platinization and then tested. The results of these tests will be omitted, because no new conclusions could be drawn from them. The cells when lightly platinized showed the

TABLE VIII
CELL DIMENSIONS

Dimensions of the new cells				Electrodes			
Cell	Cell constant	Diam. inside, cm.	Distance between electrodes, cm.	Diam. of disk, cm.	Thick of disk, cm.	Diam. of rod, cm.	Length of rod, cm.
K	0.67503	1.8	1.5	1.4	0.033	0.011	1.6
L	2.6268	1.6	6	1.3	.033	.011	1.6
M	11.7066	1.0	11.5	2.3	.033	.011	2.0
N	126.722	0.33	16.5	1.9	.025	.011	2.0

characteristic behavior of cells in which errors due to polarization are present even up to high resistances. The cells were then given a heavy platinization, using a platinizing solution containing a trace of lead acetate.

TABLE IX
CELL COMPARISON DATA. CELL K. (KCl AS ELECTROLYTE)
Heavy Platinization

	KCl	$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$		
Soln.	Approx. concn.	R	C_p μμf.	$C_p\omega R =$ tan θ	R	C_p μμf.	$C_p\omega R =$ tan θ
41	0.0001	57,066.6	14	0.0025	57,060.0	12	0.0047
43	.0003	15,982.7	18	.00090	15,981.0	17	.0018
44	.0003	13,847.3	20	.00087	13,846.1	17	.0016
42	.0005	9,762.1	17	.00052	9,761.4	11	.00073
45	.0009	5,344.66	23	.00038	5,344.16	14	.00051
46	.0016	2,891.94	43	.00039	2,891.63	20	.00040
47	.0035	1,346.72	90	.00038	1,346.55	38	.00035
48	.0075	662.13	200	.00042	662.03	75	.00034
49	.017	294.253	700	.00065	294.204	210	.00042
50	.03	158.106	1400	.00069	158.076	480	.00052
51	.07	75.664	4300	.00102	75.653	1325	.00069
52	.2	30.009	21500	.00203	30.005	4900	.00101

	$f = 2280$ $\omega = 14326$			$f = 3000$ $\omega = 18850$			$f = 4000$ $\omega = 25133$		
Soln.	R	C_p μμf.	$C_p\omega R =$ tan θ	R	C_p μμf.	$C_p\omega R =$ tan θ	R	C_p μμf.	$C_p\omega R =$ tan 0
41	57,050.1	12	0.0098	57,044.1	12	0.0192	57,036.1	12	0.0172
43	15,979.0	15	.0034	15,978.5	15	.0045	15,977.5	15	.0060
44	13,844.8	17	.0034	13,844.2	17	.0044	13,843.6	18	.0063
42	9,760.8	10	.0014	9,760.6	9	.0017	9,760.4	9	.0022
45	5,343.66	12	.00092	5,343.4	11	.0011	5,343.2	11	.0015
46	2,891.42	14	.00058	2,891.35	13	.00071	2,891.26	12	.00087
47	1,346.42	21	.00041	1,346.39	18	.00046	1,346.35	17	.00057
48	661.95	33	.00031	661.93	23	.00029	661.90	18	.00030
49	294.151	90	.00038	294.136	70	.00038	294.123	55	.00041
50	158.044	200	.00045	158.034	140	.00041	158.026	100	.00041
51	75.638	550	.00060	75.632	400	.00057	75.626	300	.00057
52	30.001	1200	.00052	29.999	670	.00038	29.997	300	.00023

The cells were filled with common solutions of potassium chloride and the resistance and capacitance of each measured as before, except that the readings were taken not only with 1090 and 2280 cycles, but also with 500, 3000, and 4000 cycles as well. The results are recorded in Tables IX to XII. A consideration of the values of tan θ at high resistances indicates that cell K, in which the electrodes are 1.5 cm. apart, is superior to cells II and IV, about the same as cells I and V, and inferior to cell III. In cell K the electrodes are comparatively close together, but the disadvantage of this close proximity is partly avoided by the design which places the filling tubes outside the contact tubes (see Fig. 14). The separation of electrodes and filling tubes is apparently inadequate in this cell. In this cell the capacitance which makes trouble is probably that between the portion of the cell between the electrodes and the filling tubes and contact tubes.

TABLE X

CELL COMPARISON DATA. CELL L. (KCl AS ELECTROLYTE)

Heavy Platinization

		f = 500 ω = 3142			f = 1090 ω = 6849		
Soln.	Approx. concn.	R	C_P μμf.	$C_P\omega R =$ tan θ	R	C_P μμf.	$C_P\omega R =$ tan θ
44	0.0003	53,876.3	4	0.00068	53,872.0	4	0.0015
42	.0005	37,985.6	5	.00060	37,982.8	5	.0013
45	.0009	20,796.3	7	.00046	20,795.3	6	.00085
46	.0016	11,253.7	11	.00039	11,253.2	9	.00070
47	.0035	5,240.5	6	.000099	5,240.29	3	.00011
48	.0075	2,576.47	20	.00016	2,576.33	8	.00014
49	.017	1,144.88	50	.00018	1,144.83	18	.00014
50	.03	615.151	110	.00021	615.116	38	.00016
51	.07	294.378	370	.00034	294.360	120	.00024
52	.2	116.751	1900	.00070	116.744	480	.00038
53	.5	49.906	10400	.00163	49.900	2430	.00083
54	1.0	25.195	37000	.00293	25.184	8100	.00140

	f = 2280 ω = 14326			f = 3000 ω = 18850			f = 4000 w = 25133		
Soln.	R	C_P μμf.	$C_P\omega R =$ tan θ	R	C_P μμf.	$C_P\omega R =$ tan θ	R	C_P μμf.	$C_P\omega R =$ tan θ
44	53,867.3	4	0.0031	53,864.7	4	0.0040	53,861.6	4	0.0054
42	37,980.7	5	.0027	37,979.1	5	.0036	37,977.6	4	.0038
45	20,794.4	6	.0018	20,794.0	6	.0023	20,793.6	6	.0031
46	11,252.8	8	.0013	11,252.5	8	.0017	11,252.4	7	.0020
47	5,240.04	3	.00022	5,240.03	3	.00029	5,239.88	3	.00040
48	2,576.23	5	.00018	2,576.20	4	.00019	2,576.19	3	.00019
49	1,144.79	9	.00015	1,144.76	7	.00015	1,144.74	5	.00015
50	615.079	14	.00012	615.061	10	.00012	615.049	6	.00009
51	294.339	55	.00023	294.333	38	.00021	294.327	32	.00024
52	116.738	160	.00027	116.734	120	.00026	116.730	70	.00021
53	49.896	760	.00054	49.895	530	.00050	49.895	400	.00050
54	25.182	1750	.00063	25.181	900	.00042	25.180	420	.00027

TABLE XI

CELL COMPARISON DATA. CELL M. (KCl AS ELECTROLYTE)

Heavy Platinization

		$f = 500$ $w = 3142$			$f = 1090$ $w = 6849$		
Soln.	Approx. *concn.*	*R*	C_P $\mu\mu$f.	$C_P\omega R =$ *tan 0*	*R*	C_P $\mu\mu$f.	$C_P\omega R =$ *tan 0*
46	0.0016	50,156.1	0	0	50,154.9	0	0
47	.0035	23,354.9	3	0.00022	23,354.5	3	0.00047
48	.0075	11,482.0	6	.00022	11,482.1	6	.00047
49	.017	5,102.2	0	0	5,102.20	0	0
50	.03	2,741.25	0	0	2,741.26	0	0
51	.07	1,311.76	8	.000033	1,311.77	3	.000026
52	.2	520.277	38	.000062	520.270	9	.000032
53	.5	222.399	190	.000133	222.392	55	.000083
54	1.0	112.261	720	.000254	112.259	170	.00013
55	3.0	38.257	6300	.00076	38.254	1425	.00037

	$f = 2280$ $\omega = 14326$			$f = 3000$ $\omega = 18850$			$f = 4000$ $\omega = 25133$		
Soln.	*R*	C_P $\mu\mu$f.	$C_P\omega R =$ *tan 0*	*R*	C_P *f .*	$C_PR =$ *tan 0*	*R*	C_P $\mu\mu$f.	$C_P\omega R =$ *tan 0*
46	50,154.6	0	0	50,154.6	0	0	50,154.6	0	0
47	23,354.2	3	0.0010	23,353.7	3	0.0013	23,353.8	3	0.0018
48	11,481.8	6	.00099	11,481.7	6	.0013	11,481.8	6	.0017
49	5,102.1	0	0	5,102.2	0	0	5,102.2	0	0
50	2,741.23	0	0	2,741.24	0	0	2,741.2	0	0
51	1,311.77	3	.000056	1,311.76	3	.000075	1,311.76	3	.000098
52	520.265	0	0	520.261	0	0	520.266	0	0
53	222.389	19	.000060	222.392	12	.000050	222.391	7	.000039
54	112.256	38	.000061	112.255	22	.000046	112.254	9	.000025
55	38.253	320	.000175	38.253	180	.000130	38.253	90	.000086

We infer that in cells having electrodes as close together as this it would have been better to extend the filling and contact tubes in the direction of the axis of the cell for several centimeters before bending them upward.

Cell L, in which the electrodes are 6 cm. apart, shows a definite improvement over all of our older cells in having a lower phase angle at high resistances than any of the older cells. Nevertheless, cell L does have a measurable parallel capacitance at high resistances and therefore a slight although reduced error due to capacitative shunt.

However, in cells M and N, in which the separation of the electrodes is 11.5 and 16.5 cm., respectively, the parallel capacitance is so low that it is no longer measurable with our bridge, since it is of the same order of magnitude as the unavoidable capacitance in bridge, boxes, lead wires and in the condensers at their zero setting. Readings of less than 5 micromicrofarads have little significance in our apparatus. But these capacitance readings, in spite of their lack of precision, do prove that cells M and N have a lower phase angle at high resistances than any of the other cells and therefore by

TABLE XII

CELL COMPARISON DATA. CELL N. (KCl AS ELECTROLYTE)

Heavy Platinization

		$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$		
Soln.	**Approx** concn.	R	C_P $\mu\mu$f.	$C_P\omega R =$ tan θ	R	C_P $\mu\mu$f.	$C_P\omega R =$ tan θ
49	0.017	55,225	0	0	56,224	0	0
50	.03	29,672.6	0	0	29,671 S	0	0
51	07	14,199.2	*3*	0 00013	14,199.0	3	0.000284
52	.2	5,631 9	0	0	5,631.8	0	0
53	5	2,407 8	2	.000015	2,407.65	0	0
54	1.0	1,215.25	15	.000051	1,215.25	0	0
55	3 0	414.23	140	.00018	414.225	29	0 000082

	$f = 2280$ $\omega = 14326$			$f = 3000$ $\omega = 18850$		$f = 4000$ $\omega = 25135$	
Soln.	R	C_P $\mu\mu$f.	$C_P\omega R =$ tan θ	R	C_P $\mu\mu$f.	R	C_P $\mu\mu$f.
49	55,221	0	0	55,221	0	55,221	0
50	29,670.9	0	0	29,670.5	0	29,670.3	0
51	14,198.8	3	0.00061	14,198.6	3	14,198.5	3
52	5,631.8	0	0	5,631.9	0	5,631.9	0
53	2,407.65	0	0	2,407.65	0	2,407.65	0
54	1,215.25	0	0	1,215.25	0	1,215.25	0
55	414.218	8	0.000048	414.218	3	414.216	0

virtue of Equation 17 the error due to capacitance shunt has been greatly reduced and probably made negligible.

A surer test of the quality of the new cells is the variation in the apparent resistance with variation in frequency, because this is not dependent on the capacitance measurements of low precision. It will be recalled that with the old cells the variation of resistance with frequency increased rapidly with the resistance being measured and at about 50,000 ohms a change in the frequency from 1090 to 2280 cycles caused the following decreases in resistance: cell I, 133.5 ohms; II, 96 ohms; III, 37 ohms; IV, 58.4 ohms. These figures may be compared with the corresponding values for the new cells: cell K, 9.9 ohms; cell L, 4.3 ohms; cell M, 0.3 ohm: cell N, **3** ohms. When the frequencies increased to 4000, cell K shows a further drop of 4 ohms, cell L of 6 ohms and cells M and N are unchanged.

It is apparent that the effect of variation in frequency has been greatly reduced in the new cells and the effect which remains is not proportional to the square of the frequency, which has been demonstrated to be characteristic of errors due to a capacitative shunt. The slight remaining frequency effect must therefore be ascribed to some other cause, probably polarization.

Attention is called especially to cell M, which shows an apparent variation between 1090 and 4000 cycles of only **0.3** ohm which is less than

0.001%. An error of this magnitude might be caused by a change in temperature of less than 0.0005°. The change of 1.2 ohms in cell M between 500 and 1090 cycles is probably due to some polarization at the lower frequency. It may therefore be regarded as established that there is no real change in the conductance of electrolytes with a change in frequency up to 4000 cycles. The slight frequency effect remaining in the other new cells and the much greater frequency effect reported by other experimenters is due to errors caused by polarization or faulty design of bridge or cells.

Debye and Falkenhagen[22] have made a theoretical study of the effect of variation in frequency on the conductance of dilute solutions based on the Debye–Hückel interionic attraction theory of electrolytes. One of the most important theoretical deductions of Debye and Hückel is that the electric forces between the ions tend to maintain a space lattice structure and oppose the motion of an ion under the influence of an outside electric field and thus cause a decrease in conductance which is proportional to the square root of the concentration. Debye and Falkenhagen conclude that at extremely high frequencies the influence of the interionic forces in retarding the motion of an ion in an electric field tends to disappear, so that the conductance increases with increasing frequency. Thus, for example, with 0.001 N potassium chloride solution and a wave length of 14.9 meters, corresponding to a frequency of 20 million cycles per second, the retardation by the interionic attraction is reduced to one-half of its value at zero frequency.[23] Falkenhagen and Williams[24] have reviewed the paper referred to and interpreted it by the computation of numerical values for numerous specific cases as a function of the mobility and valence of the ions, the concentration, temperature, nature of solvent, and the frequency. It is apparent from this analysis that the theory predicts no measurable change of conductance with variations in frequency within the audio range. Neither of these papers contains any experimental verification of the theoretical deductions.

Sack,[25] in a brief preliminary notice, claims to have demonstrated the variation of resistance with variation of frequency at frequencies from 6 million to 20 million cycles but the effect is not much, if any, greater than the experimental errors in the method.

A third test of the quality of the cells is the constancy of the cell resistance ratios. These ratios are not given here since they may be computed readily by anyone interested, from the data in Tables IX to XII; they are shown in Fig. 15. These ratios are much more nearly constant than those

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[22] P. Debye and H. Falkenhagen, *Physik.* Z., 29, 121 (1928).

[23] Debye and Falkenhagen, Ref. 22, p. 131.

[24] H. Falkenhagen and J. W. Williams, J. *Phys.* Chcm., 33,1121 (1929).

[25] H. Sack, *Physik.* Z., 29, 627 (1928).

given by any of the older cells. Considering only the values at resistances above 1000 ohms in order to avoid the effects of polarization, it will be seen that the Parker Effect has been substantially eliminated with the new cells. The ratio of L to M and of M to N remains within 0.01% of the mean except at the lower resistances, where the tan 8–log R curves show that polarization plays a part. The elimination of the Parker Effect by the avoidance of capacitative shunt in the design of the cells furnishes additional evidence as to the validity and usefulness of our new theory that the Parker Effect is due to the shunt. This test agrees with the first two tests in showing that cell K is not quite so good as the others.

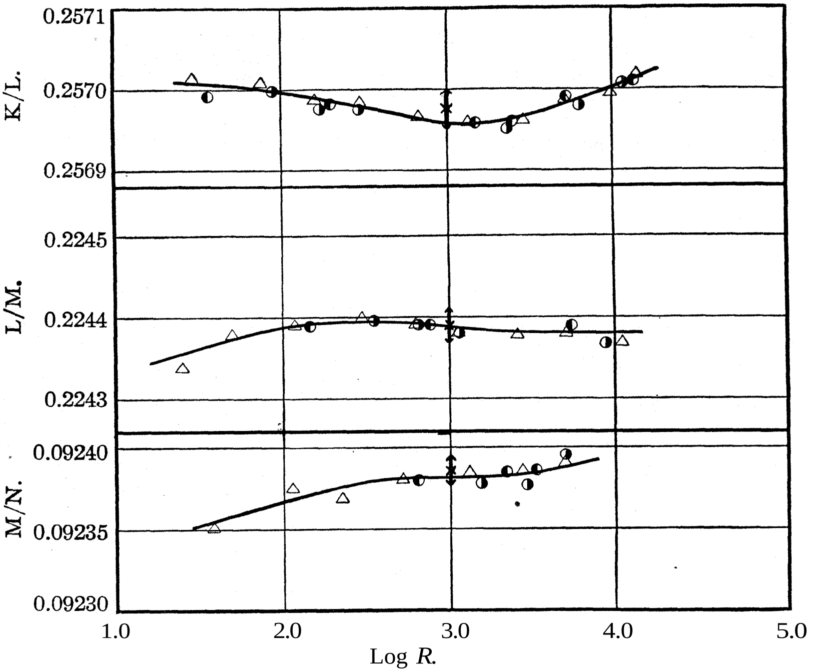

Fig. 15.—A, KCl; ◐, Na_2SO_4; ◑, $Ba(NO_3)_2$.

Effect of Change of Electrolyte.—It now remains to compare the behavior of other electrolytes with that of potassium chloride. For this purpose we have selected barium nitrate and sodium sulfate because Randall and Scott have reported experiments with these salts which they interpret as showing a specific effect of the salt used. We, therefore, made a series of cell comparisons using these two salts, similar to those reported above with potassium chloride, although less extensive. The results are shown in Tables XIII to XVI.

We have plotted the tan θ–log R curves (although they are not reproduced here) and find that the points fall on the same curves as the data

TABLE XIII

CELL COMPARISON DATA. CELL K

Heavy Platinization

Soln.	Approx. concn. Na_2SO_4	$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$			$f = 3000$ $\omega = 18850$		
		R	C_P μμf.	$C_P\omega R =$ tan θ	R	C_P μμf.	$C_P\omega R =$ tan0	R	C_P μμf.	$C_P\omega R =$ tan θ
56	0.0002				13,249 9	15	0.00136			
60	.0005	5317.35	22	0.00037	5,316 80	13	,00047	5316.50	10	0.0010
59	,001				2,505.78	18	.00031			
58	.002	1472.71	86	.00040	1,472 56	36	.00036	1472.39	17	.00047
57	.018	193.496	1075		193.462	380	.00050	193.414	110	.00040
62	.10	36.876	15000	.00065	36.873	4000	.00101	36.862	1000	.00069
	$Ba(NO_3)_2$									
67	0.0003				11,649.9	14	0 00112			
61	.0005	6379.6	20	0 00040	6,379.3	11	.00048	6378.9	9	.0011
66	.0012	2297.91	40	.00029	2,297.76	20	.000315	2297.41	10	.00043
65	.01				290.059	190	.00038			
64	.02				169.262	420	,00049			
63	.04	88.878	3000	.00084	88.869	1000	.00061	88.848	320	.00054

TABLE XIV

CELL COMPARISON DATA. CELL L

Heavy Platinization

Soln.	Approx. concn. Na_2SO_4	$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$			$f = 3000$ $\omega = 18850$		
		R	C_P μμf.	$C_P\omega R =$ tan θ	R	C_P μμf.	$C_P\omega R =$ tan θ	R	C_P μμf.	$C_P\omega R =$ tan θ
56	0.0002				51,554	4	0.0014			
60	.0005	20,689.5	7	0.00046	20,688.6	6	.00085	20,687.7	6	0.0023
59	.001				9,751.6	3	.00020			
58	.002	5,731.00	6	.000109	5,730.75	4	,00016	5,730.55	3	.00033
57	.018	752.85	95	.000224	782.82	27	.00014	752.74	6	.000085
62	.10	143.483	1300	.000585	143.479	340	.00033	143.466	300	.00082
	$Ba(NO_3)_2$									
67	0.0003				45,329.0	5	0.00155			
61	.0005	24,825.1	6	0.00047	24,824 1	5	,00085	24,822.9	5	0.0023
66	.0012	8,943.0	0	0	8,942.4	0	0	8,942.4	0	
65	.01	1,128.70	15	.000053	1,128.74	28	.00022	1,128.67	2	.000043
64	.02				658.669	30	.00014			
63	.04	345.812	240	.00026	345.797	75	.000178	345.780	25	.00016

obtained with potassium chloride. The cell resistance ratios for all three salts also were found to be alike within 0.01%, as is shown in Fig. 15. With none of the three salts is there any variation in resistance with variation in frequency from 1090 to 3000 cycles per second greater than 0.01%. We conclude, therefore, that the hypothesis, first suggested by Parker and later supported by Randall and Scott, that adsorption is responsible for the Parker Effect is without a sound theoretical or experimental basis and is unnecessary to account for the known facts. Of course, this does not preclude the possibility that a real adsorption effect may be demonstrated in the future with some other electrolyte or in extremely narrow tubes.

On the other hand, our hypothesis that the Parker Effect is due to a shunt

TABLE XV

CELL COMPARISON DATA. CELL M

Heavy Platinization

		$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$			$f = 3000$ $\omega = 18850$		
Soln.	Approx. concn., Na_2SO_4	R	C_P $\mu\mu f.$	$C_P\omega R =$ $\tan\theta$	R	C_P $\mu\mu f.$	$C_P\omega R =$ $\tan\theta$	R	C_P $\mu\mu f.$	$C_P\omega R =$ $\tan\theta$
59	0.001				43,461.5	0				
58	.002	25,540.4	6	0.00049	25,539.9	4	0.00069	25,539.9	3	0.0015
57	.018	3,355.02	0	0	3,355.02	0		3,355.02	0	
68					2,205.62	1	.000015			
62	.1	639.440	25	.000051	639.444	4	.000017	639.440	4	.000048
	$Ba(NO_3)_2$									
66	0.0012	39,857.5	0	0	39,856.0	0	0	39,856.3	0	0
65	.01				5,030.54	0	0			
64	.02				2,935.38	0	0			
63	.04	1,541.02	8	.000039	1,541.01	0	0	1,540.97	0	0

TABLE XVI

CELL COMPARISON DATA. CELL N

Heavy **Platinization**

		$f = 500$ $w = 3142$		$f = 1090$ $\omega = 6849$		$f = 3000$ $w = 18850$
Soln.	Approx. concn., Na_2SO_4	R	C_P $\mu\mu f.$	R	C_P $\mu\mu f.$	R
57	0.018	36,315.9	0	36,315.3	0	36,313.0
68				23,874.2	0	
62	.1	6,921.9	0	6,921.86	0	6,921.8
	$Ba(NO_3)_2$					
65	0.01			54,445.8	0	
64	.02			31,776.1	0	
63	.04	16,681.7	3	16,681.6	0	16,682.6

across the electrodes containing resistance and capacitance is in accord with all of the known facts. It has led to an equation for the error due to the shunt which has been confirmed quantitatively as to the influence of frequency and capacitance on the error and has guided the design of a new type of cell in which capacitance between parts of the cell of opposite polarity is made negligible, with the result that the new cells have a very low phase angle and show no Parker Effect and no variation of resistance with frequency.

Acknowledgment.—Grateful acknowledgment is made for an appropriation from the Bache Fund of the National Academy of Sciences and from the Milton Fund of Harvard University for the expenses of this work.

Summary

1. The observation of Parker that the ratio of the resistances of two conductance cells when filled with a common solution and measured with an alternating current bridge is not independent of the specific conductance of the solution used, has been confirmed experimentally with cells of the type commonly used. The curves obtained are, however, of simpler form than those obtained by Parker and this simplification of the problem is ascribed to the use of a superior bridge, thus avoiding some causes of error present in Parker's work.

2. By using an unshielded bridge carefully designed to avoid inductance and capacitance, the phase angle between the current and the voltage in conductance cells has been measured and made significant in the study of errors in conductance measurements and in the design of cells. The phase angle in the cells depends on the frequency used, the resistance being measured, the degree of platinization, and the dimensions of the cell.

3. The conclusion of earlier investigators that the error due to polarization is positive in sign and can be minimized and made practically insignificant by a combined use of proper platinization, large electrodes, high frequency, and high resistance, is confirmed.

4. It is demonstrated for the first time that with cells of the type commonly used there is a capacitative shunt between parts of the cell of opposite polarity, which has the effect of making the measured resistance lower than the true resistances of the electrolyte between the electrodes.

5. By the use of alternating current theory the error due to the capacitative shunt is shown to be approximately AR $= -R_P R_T^2 \omega^2 C_P^2 = -R_P \tan^2 \theta$. The validity of this equation has been demonstrated by special experiments. The error due to capacitative shunts differs from that due to polarization in sign and in being increased by an increase in the frequency used and in the resistance being measured. The error due to capacitative shunt varies as the square of the capacitance in the shunt and as the first power of the resistance in the shunt whereas neither of these influences the error due to polarization. On the other hand, the degree of platinization, which has a great influence on the polarization, is without influence on the error due to capacitative shunt.

6. The equation for the error due to capacitative shunt has guided the design of new cells in which close proximity of parts of the cell of opposite polarity is avoided.

7. It has been demonstrated by measurements of phase angle and by intercomparisons of cells that the new cells are greatly superior to the forms commonly used. The new cells can be used at frequencies and resistances so high as to make errors due to polarization negligible without introducing errors due to capacitative shunt so that results which seem to be reliable within 0.01% may be obtained with them.

8. Although earlier experimenters have reported a variation in the conductance of electrolytes with change in frequency, it has been demonstrated experimentally that no change greater than a few thousandths of one per cent. occurs between the limits of 1090 and 4000 cycles per second when errors due to polarization and capacitative shunt are avoided.

9. The most convenient test of the quality of cells is the observation of the variation in apparent resistance with variation in frequency.

10. It has been shown experimentally that the ratio of the resistances of a pair of cells when filled with a common solution is independent of the electrolyte used for three different electrolytes, This does not confirm observations of earlier experimenters and removes the only experimental support for the hypothesis of Parker that adsorption is responsible for the Parker Effect.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF RUTGERS UNIVERSITY]

THE VAPOR PRESSURE OF PYRIDINE[1]

BY P. A. VAN DER MEULEN AND RUSSELL F. MANN

RECEIVED OCTOBER 18, 1930 PUBLISHED FEBRUARY 9, 1931

In the course of a study of certain complex compounds containing pyridine, a search made of the literature revealed that the vapor pressure curve of this substance below the normal boiling point has been only partially determined. Kahlbaum[2] determined the vapor pressure at six temperatures below 51°. Zawidzki[3] reports a single value at 80°; the "International Critical Tables"[4] give the boiling point as 115.3°, but the vapor pressure as 760 mm. at 115.50°.[5,6] The present study was undertaken to fill the gaps between these data.

Experimental Work

Pyridine C. P. brand of Baker was purified as recommended by Arndt and Nachtwey.[7] This involves preparation of the pyridine perchlorate, purification of the perchlorate by crystallization, and liberation of the pyridine. The product was dried over solid potassium hydroxide, and was distilled with a fractionating column. The first and last quarters were rejected. The middle fraction, passing over between 115.1 and 115.3° was collected. This was redistilled as required.

The apparatus used was similar to that employed by Mortimer and Mur-

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[1] This paper is based on a thesis submitted by Russell F. Mann to the faculty of Rutgers University in partial fulfilment of the requirements for the degree of Master of Science.

[2] G. W. A. Kahlbaum, "Siedetemperatur und Druck," Leipzig, *1885*, p. 67.

[3] J. v. Zawidzki, *Z. physik. Chem., 35, 129–203 (1900).*

[4] "*I. C. T.*," McGraw-Hill Book Co., Inc., New York, *1926*, Vol. I, *p.* 190.

[5] *Ibid., 1928,* Vol. III, p. *219.*

[6] K. G. MacKensie, *Ind. Eng. Chem., 1, 360–362* (1909); Robert Schiff, *Ber., 19, 560–568 (1886); W.* Louguinine, *Compt. rend.,* **129,** 366–369 (1899); *H.* Hartley, N. G. Thomas and M. P. Appleby, J. *Chem. Soc. (Trans.),93,* 538–563 *(1908); W. R.* Innes, *ibid., 79, 261–266 (1901); E. J.* Constam and J. White, *Am. Chem.* J.,*29, 1-49 (1903):* J. v. Zawidzki, *Chem.-Ztg., 30,299 (1906).*

[7] F. Arndt and P. Nachtwey, *Ber.,* **59A,** 448–455 *(1926).*

phy[8] in their modification of the static isoteniscope method of Smith and Menzies.[9] The apparatus was checked against the values for the vapor pressure of water given by Holborn and Henning.[10]

The isoteniscope was attached to the apparatus by means of a slip joint provided with a mercury seal, making possible the removal of this portion of the apparatus for the purpose of cleaning and filling. For temperatures above 25° a four-liter beaker surrounded by an asbestos sheath provided with peep holes was used as a constant temperature bath. A white mineral oil served as the bath liquid. Below 25° a wide-mouthed Dewar flask of clear glass was employed as a thermostat. The liquid was chilled ether. It was found necessary to use two high-speed propeller-type stirrers to maintain a uniform temperature throughout the bath. All thermometers used in this work were standardized by means of a Reichsanstalt standard thermometer. The manometer was of the ordinary open-end type, 7 mm. wide, securely mounted on a brick wall, and shielded from the heat of the bath. All manometer readings were made with a cathetometer, as were also readings of the levels in the U-arm of the isoteniscope. Manometer and barometer readings were reduced to mm. of mercury at 0°. A brass scale correction for the barometer was necessary.

Manipulation.—For each set of determinations the detachable isoteniscope arm was thoroughly cleaned, and pyridine was redistilled directly into this portion of the apparatus. The isoteniscope was then immersed in a bath of solid carbon dioxide and ether to chill the pyridine, and the apparatus was pumped out with a Hy-vac oil pump. Pumping was continued for one-half hour. A portion of the sample was then allowed to distil over into the U-tube. As an open-end manometer was used throughout the experiment, readings were not made below $-15°$, since at lower temperatures the pressure was less than 1 mm.

Determinations were continued up to and slightly above the normal boiling point of pyridine, a complete series of determinations being made at one time. Several samples of pyridine were used for the pressure determinations and a sufficient number of checks were made to insure the accuracy of the results.

Experimental Data.—In order to secure a suitable empirical equation we followed the lead of Antoine,[11] Cox,[12] and Davis,[13] and adopted the empirical equation

$$\text{Log } p = A - \frac{B}{t + 205}$$

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[8] F. Spencer Mortimer and R. V. Murphy, *Ind. Eng. Chem*, *15,* 1140–1142 (1923).

[9] Alexander Smith and A. W. C. Menzies, THIS JOURNAL, 32,1412–1434 (1910).

[10] L. Holborn and F. Henning, *Ann. Physik,* [4] 26, 833–883 (1908).

[11] Chwolson, "Hehrbuch der Physik," Vol. III, 3d German ed., 1905, p. 741.

[12] Edwin R. Cox, *Ind. Eng. Chem.,* 15,592–593 (1923).

[13] D. S. Davis, *ibid.,* 17, 735 (1925); 22, 380–381 (1930).

The best values for A and B were then calculated by the method of least squares from our fifty vapor pressure determinations between −15 and +116° The resulting equation is

$$\text{Log } p = 6.8827 - \frac{1281.3}{t + 205}$$

where p is expressed in mm. of mercury and t is temperature in degrees centigrade.

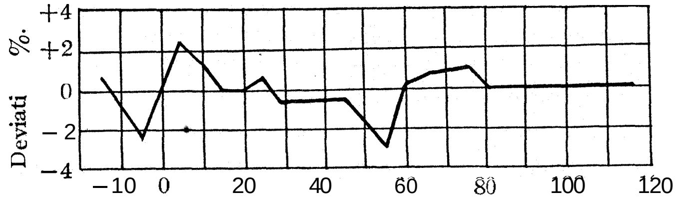

Fig. 1.

The deviations of our experimental results from this equation have been plotted in Fig. 1. The maximum deviation is 3.1%. Vapor pressures at round temperatures calculated from this equation are given in Table I.

TABLE I

VAPOR PRESSURE OF PYRIDINE AT ROUND TEMPERATURES

Temperature, °C.	Calculated pressure, mm.	Temperature, °C.	Calculated pressure, mm.
−20.0	0.91	60.0	111.6
−10.0	2.05	70.0	167.3
0.0	4.29	80.0	243.8
$10.0	8.38	90.0	346.3
+20.0	15.4	100.0	481
30.0	27.0	110.0	.653
40.0	45.0	115.2	760
50.0	72.1	120.0	872

Summary

Pyridine has been purified by crystallization of the perchlorate, followed by redistillation. The vapor pressure of this purified pyridine has been determined by the isoteniscope method. The relation between temperature and vapor pressure between −20 and +120° is best represented by the empirical equation

$$\text{Log } p = 6.8827 - \frac{1281.3}{t + 205}$$

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY NO. 646 AND OF VASSAR COLLEGE]

THE QUINHYDRONE ELECTRODE. I.

BY J. LIVINGSTON R. MORGAN, OLIVE M. LAMMERT AND MARGARET A. CAMPBELL

RECEIVED OCTOBER 27, 1930 PUBLISHED FEBRUARY 9, 1931

Introduction

Ever since its discovery by Haber and Russ[1] and its early development by Granger and Nelson[2] and by Biilmann,[3] the quinhydrone electrode has been a favorite substitute for the hydrogen electrode in the determination of the hydrogen-ion concentration of solutions. This early work indicated that, for moderate precision at least, the electrode is quickly and easily prepared, develops its potential almost instantaneously, does not require a gas bubbling through the solution continuously and can be used, therefore, for work on body fluids containing dissolved carbon dioxide, and is not affected by atmospheric pressure; moreover, it can be used in solutions in which the reducing effect of hydrogen, or of hydrogen and platinum black, prohibits the use of the usual hydrogen electrode. In view of the ease with which the electrode can be prepared, the fact that the electrodes deteriorate in a comparatively short time constitutes only a minor objection. The real limitation of the electrode lies in the fact that even for work of moderate precision the electrode cannot be used in alkaline solutions above a PH of 8.5, particularly in the presence of oxygen.

Preliminary to some work on polarization which demanded a standard electrode of constant potential in acid solution, we undertook a study of the quinhydrous electrode, since it could be connected to the electromotive chain without the introduction of liquid junction potentials. Up to the time that this investigation was initiated, little work had been done from the point of view of the reproducibility of the electrode with a precision greater than 0.0001 volt; the interest of previous investigators lay primarily in the theory of the reaction producing the electrode, in the values of its potential compared to the well-known standard electrodes, in its salt error, and in the design of new forms of electrode for particular applications.

Since that time, however, the work of Biilmann and Jensen[4] has appeared. These investigators studied the reproducibility of the electrode and its value compared to the hydrogen electrode, their measurements being reported to 0.00001 volt. However, inasmuch as our method of attack differed from theirs, and inasmuch as their work was limited to a study

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[1] Haber and Russ, Z. *physik. Chem.*, *47,* 257 (1904).

[2] Granger and Nelson, THIS JOURNAL, 43, 1401 (1921).

[3] Biilmann, *Ann. chim.,* [9] *15,* 109 (1921).

[4] Biilmann and Jensen, *Bull. soc. chim., 41,* 151 (1927).

with comparatively few electrodes and did not cover many of the controversial points, it seemed wise to continue the research.

We confined the first part of our work to the reproducibility of the electrode since its actual value was of no immediate interest to us. With the hope of reproducing conditions in different laboratories we selected for the base of our electrodes a variety of metals: gold, platinum, platinum--iridium alloy, platinum–rhodium alloy, old platinum which was roughened by repeated platinization and deplatinization, having been used for years as hydrogen electrodes, and new platinum purchased at different times from different companies, platinum and gold wires of different cross sections and lengths and foils of different areas. All in all we used 194 electrodes cut into different sizes from **37** different pieces of metal with the result that we had groups of four to six electrodes, the electrodes within a group being as nearly identical as we were able to make them. A total of 3299 cells were prepared by combining these electrodes in pairs and on these cells more than 8000 measurements of the potential differences were made under varying conditions. Obviously a summary of such a large number of determinations is difficult but is attempted in view of the very general usefulness of the electrode, because of the precision with which the electrode may be prepared, and in view of the fact that there are so few data given in the literature to substantiate the preferences of different investigators as to the metal to be used as a base and as to the method of preparation of the electrode and solution.

In this paper we shall report the results of our work on the method of preparation of the metal electrode, on the method of cleaning and drying the electrodes, on the method of preparation of the quinhydrone solution, and on a comparison of the reproducibility possible with electrodes of different sizes and compositions for measurements made in the presence of air. In other papers to follow we shall present results on the reproducibility possible when the air is replaced by nitrogen, on a comparison of the potentials developed in quinhydrone solutions by electrodes of different sizes arid compositions, both in air and in nitrogen, on the behavior of the electrode prepared in solutions other than in 0.1 N hydrochloric acid, and on the electromotive force of the quinhydrone compared with other well-known half-cells. Much of the material for these papers is at hand; however, in view of the fact that some time must elapse before the data and compilations can be completed, it seems wise to make this preliminary report for the benefit of any who wish to use the electrode under the conditions described in this paper.

Preparation **and** Purification of Materials.—Several lots of quinhydrone, purchased from Eastman Kodak Co., and melting at 169–170° were used. The water and ethyl alcohol used were redistilled; the air for drying the electrodes **was** compressed by a water pump and conducted through dilute sulfuric acid, distilled water, soda lime and calcium chloride; the cleaning mixture was prepared from *c.* P. chemicals.

Apparatus

The electromotive force measurements, made in the usual manner with a Leeds and Northrup, Type K, potentiometer and a Type R, No. 2500 e, galvanometer, are believed to be precise to 0.000001 volt, since the usual precautions as to shielding,[5] temperature control and thermoelectric effects have been taken,

Electrode Vessel.—A 600-cc. pyrex beaker fitted with a wood and cork stopper was used as electrode vessel. In each stopper was inserted seven lengths of glass tubing which extended about 5 cm. below the stopper and about 2.5 cm. above. Six of these tubes carried the electrodes and prevented them from touching one another in the solution; the seventh carried the motor-driven stirrer.

Electrodes.—Wires and foils were sealed, with the aid of sealing-in glass, into a piece of glass tubing. Connections with the potentiometer wires were made in some cases with mercury, in other cases, when longer wires were used, directly with a wire connector. Each electrode tube was supplied with a cork stopper fitting the glass tube in the cover of the electrode vessel. A more detailed description of the electrodes is as follows.

Small Wires.—0, Nos. 1–6; Pt, 7–12; Ir, 7–12; Rh, 7–12; Au, 7–12. (Approximately 0.38 mm. in diameter and 1.5 cm. in length.) ***Series O,*** six electrodes cut from same piece of new C. P. platinum. ***Series Pt,*** six from same piece of new C. P. platinum different from O. ***Series Ir,*** six from same piece new platinum–iridium, 10% alloy. ***Series Rh,*** six from same piece new platinum–rhodium, 10% alloy. ***Series Au,*** six from same piece new 24K gold.

Large Wires.—A, Nos. 1–6; B, 1–6; Pt, 1–6; Ir, 1–6; Rh, 1–6; Au, 1–6; St, 1–6. (Approximately 1 mm. diameter, 2 cm. length.) ***Series A,*** six pieces of old platinum of unknown composition which had been around the laboratory for years and which, just previous to this work, had been used for hydrogen electrodes. ***Series B,*** six electrodes of old platinum but cut from same piece of wire. History similar to A. ***Series Pt,*** new C. P. platinum, six from same piece. ***Series Ir,*** six from new piece platinum–iridium, 10% alloy. ***Series Rh,*** six from new piece platinum–rhodium, 10% alloy. ***Series Au*** and ***Series St,*** six electrodes in each series from each of two new pieces of 24K gold.

Special Wires (Am Pt, Nos. 1–6 and L & N, Nos. 1–4) ***Series Am Pt*** (0.60 mm. × 2 cm.) six electrodes cut from the same piece of new C. P. platinum wire bought of the American Platinum Co., and recommended by Cullen.[6]

Series L & N.—Four gold electrodes bought from Leeds and Northrup and described by Parker and Greer.[7]

Aside from the short wire electrodes described, sets of electrodes, usually of six each, were made from the same pieces of metal but cut into 15-cm. lengths and the middle portion of the wire covered with glass tubing. The same length of electrode was exposed to the solution and a similar length exposed at the other end of the tubing which carried the wire connector. These electrodes are described as "long."

Foils.—D-F and I-N (old); P and G (new). ***Series D-F*** (approximately 1 X 2 cm.) and ***Series I-N*** (approximately 2 × 2 cm.) six pieces of each size whose age, history and compositions are unknown; had been used as hydrogen electrodes. ***Series P:*** Twenty platinum foil electrodes cut from the same piece of new C. P. platinum foil: 4 foils each size: P_{11-1}-P_{11-4} (1 X 1 cm.); P_{12-1}-P_{12-4} (1 X 2 cm.); P_{13-1}-P_{13-4} (1 X 3 cm.); P_{22-1}-P_{22-4} (2 X 2 cm.); P_{23-1}-P_{23-4} (2 X 3 cm.). ***Series G:*** Twenty gold foil electrodes cut from the same piece of new 24K gold foil: 4 foils each size: G_{11-1}-G_{11-4}

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[5] White, THIS JOURNAL, **36,** 2011 (1914).

[6] Cullen, *J. Biol. Chem.*, **83,** 535 (1929).

[7] Parker and Greer, *Trans. Am. Electrochem. Soc.*, 49, 451 (1926).

(1 × I cm.); G_{12-1}-G_{12-4} (1 × 2 cm.); G_{13-1}-G_{13-4} (1 X 3 cm.); G_{22-1}-G_{22-4} (2 × 2 cm.); G_{23-1}-G_{23-4} (2 X 3 cm.).

While the short platinum wires and long platinum and gold wires were sealed directly into the glass tube, the gold with the aid of a wax, the platinum foils and short wire gold electrodes and foils were sealed to platinum wire which was then sealed into the glass. For the gold–platinum joint borax was used as a flux. The two pieces of wire, very clean, were dipped into the flux and then placed end to end on a piece of charcoal. Fusion was brought about by playing a small flame from an air gas torch along the platinum until the platinum was red hot and then applying the torch to the gold. In sealing the metal into the glass the sealing-in glass was applied to the platinum wire just above the joining of the two metals and the seal made to cover this joint. In this way no platinum–gold couple touched the solution and no mercury the gold.

Procedure and Results

The method of procedure which we adopted to determine the reproducibility of the potential of the quinhydrone electrode involved, in the first place, the preparation of series of either four or six electrodes as nearly identical as possible. These electrodes were then immersed in 0.1 N hydrochloric acid containing the quinhydrone and their potential differences compared, pair by pair, under a number of varying conditions.

The Method of Preparation of the Metal Electrode.—Early in our work it became evident that by far the greatest source of error involved in the preparation of reproducible quinhydrone electrodes lay in the preparation of the metal electrode to be immersed in the quinhydrone solution. The greatest care was necessary in sealing the electrode into the glass tubing. The smallest cracks or imperfections in the seal gave rise to large variations in the voltages of the electrodes and although at times these imperfections were invisible to the eye even through a magnifying glass, inevitably sooner or later the mercury just above the seals in these troublesome electrodes became so discolored that it was obviously being attacked by the solution.

This point is well illustrated by the behavior of a cell made up of electrodes B_3 and B_4. The first day the difference in potential between the two electrodes was 0.00054 volt and became 0.00050 volt at the end of four hours. The next day, the electrodes having been cleaned and dried again, the same cell gave a difference of potential of 0.07417 volt which became 0.04695 volt at the end of one and one-half hours. Finally on a third day and after another cleaning process this combination gave a potential of 0.05577 volt which finally dropped to 0.03607 volt. When electrode B_3 was measured against one of a pair of electrodes which had been giving a low potential difference its value was still very high (0.02957 volt); B_4 on the other hand gave about the same low potential as the reference electrode. B_3, exhibiting both a crack and acid attacked mercury on being examined, was remade and when next measured against B_4 gave a potential of 0.00000 volt.

Up to this point nearly all of the cells, made up of supposedly identical electrodes, had given potential differences which varied from 0.00000 volt to about 0.000030 volt. As the latter value seemed, in view of the reproducibility reported by earlier workers, too high and could not be lowered by repeated cleansing of the electrodes, all of the electrodes then in existence were remade. During this process it became obvious that the seal, which was made in the usual manner with sealing-in glass between the platinum and soft glass used, must be heated for some time in the flame and must be carefully annealed. To test the perfection of the seal the electrodes were suspended in water which was then heated to the boiling point. The electrodes were not removed until the water had cooled, when the defective ones were either cracked or the tubes filled with water. Electrodes tested in this way gave readily reproducible potentials over long periods of time even when heated for some time in very hot cleaning mixture. Of the electrodes prepared in this way and combined over a period of three years in pairs to give 3300 cells, only 29 electrodes have had to be remade because they gave potentials which were exceedingly large or did not give constant potentials in a reasonable length of time. The results just quoted apply only to those electrodes which either were not dried or were dried by some method at room temperature. When. however, the electrodes were heated directly in the flame the mortality was much greater. These points will be discussed presently.

Our observation, namely, that these imperfections and cracks in the seals were the cause of considerable variation in potential, is not new. Biilmann and Jensen,[8] Biilmann,[9] and Cullen[6] have all found difficulty with electrodes in which fissures were formed, as they were quite likely to be formed with their method of drying the electrode. However, as they give no results which indicate the magnitude of errors produced in this way, we report our results in some detail to emphasize the recommendation, originally Biilmann's,[10] that several metal electrodes be immersed in the solution for a preliminary intercomparison whenever the quinhydrone electrode is used.

Because of this difficulty with electrodes made with short wires a number of investigators prefer electrodes made with longer pieces of platinum or of gold or with pieces of a base metal welded to the noble metal. While in an investigation involving the measurement of as large a number of potentials as ours, mercury as a connecting medium proved infinitely more convenient than wire connectors, nevertheless, in an attempt to determine whether the variations in potential which, though small, still remained could be obviated by dispensing with mercury, we made a number of elec-

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[8] Biilmann and Jensen, Bull. *soc. chim* , *41,* 161 (1927).

[9] Biilmann, *ibid.*, 41, 213 (1927).

[10] Biilmann, *Trans. Faraday Soc.*, *19,* 819 (1924).

trodes with the longer wires, but with the same surface area exposed to the solution. A rather thorough examination was made of this point with a large number of small and large platinum, gold, platinum–iridium and platinum–rhodium wires, 102 long electrodes having been made and compared with the same number of short electrodes. No difference in reproducibility was found between the two types of electrodes.

The Method of Cleaning and Drying the Electrode.—A variety of methods for cleaning and drying the electrodes were tried in the first part of this work with the idea of finding some method which would give low and consistently reproducible results. We wished to replace Biilmann's[11] original method, which was to wash the electrodes with distilled water and to heat them to a red heat in an alcohol flame, by a method which would avoid the heating and consequent difficulty with cracks. In the first place we attempted to dry the electrodes with filter paper but the initial potential differences were as high as 0.00054 and 0.00071 volt and the time necessary for the electrodes to come to a constant potential difference was great. We also tried a number of cleaning mixtures besides the usual chromic acid–sulfuric acid cleaning mixture. In one case the electrodes were boiled for five minutes in 6 N potassium hydroxide, in 6 N sulfuric acid, in 6 N nitric acid and then in distilled water, the electrodes being rinsed in hot distilled water between solutions. In another case the electrodes were cleaned in a 33% alcoholic sodium hydroxide solution and then soaked in distilled water for some time. In both cases the equilibrium potential differences were very much higher than when the chromic acid cleaning mixture made of the C. P. chemicals was used. For instance one pair of electrodes gave an equilibrium potential difference of 0.00016 volt with both the $KOH–H_2SO_4–HNO_3$ and alcoholic sodium hydroxide treatment and a potential difference of 0.00002 volt with the chromic acid mixture.

Our method as finally adopted for the work reported in this paper was to submerge the electrodes in cold cleaning mixture, which was then heated to about 125° and allowed to cool to room temperature. The electrodes were usually left in the mixture overnight as a matter of convenience, although the time of treatment with the cleaning mixture seemed to be of no importance. In the morning the electrodes were rinsed with a stream of tap water, then soaked for aboat five or ten minutes in distilled and conductivity water and finally rinsed with ethyl alcohol. They were then inserted in the cork holders already described and dried in a current of purified air. About twenty minutes sufficed to dry them thoroughly. This method was very satisfactory, being convenient, not too time consuming and without the disastrous effects upon the electrodes characteristic of the heating method. The results obtained by this method are given later for a number of series of electrodes in Table I.

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[11] Biilmann, *Ann. chim.*, [9] **15**, *109* (1921).

In that table are included results obtained when the electrodes were connected in pairs during the entire process of cleaning, drying, and between measurements, as well as results obtained when the electrodes were not short circuited in this way. We made a rather extended study of this point, since it is well known that in the preparation of silver, copper or zinc electrodes two similar electrodes reach the same potential much more readily if they are short circuited in the solutions of their salts for some time prior to use. Furthermore, in the preparation of some electrodes for the measurement of the conductance of non-aqueous solutions two of us[12] learned that much more satisfactory results could be obtained if the electrodes were short circuited during the pre-treatment and drying, and in some unpublished work done in these laboratories[13] it was found that no equilibrium potential of any kind could be obtained when unplatinized platinum was used as a base for hydrogen electrodes unless the electrodes were short circuited.

In the case of the quinhydrone electrode, however, our work indicates that there is no difference in the results obtained when the electrodes are shorted or unshorted. Furthermore, in a series of six electrodes which had been shorted in pairs, potential differences of about the same magnitude were observed between two electrodes which were treated in this way as pairs, as between one electrode of one shorted pair and another electrode from another shorted pair. What we were not able to indicate in the table, however, was that with the shorted electrodes the potential differences decreased regularly until an equilibrium value was reached, when they became constant, whereas with the unshorted electrodes the potential differences sometimes, though not always, decreased to a minimum and then changed sign. This was particularly noticeable with the small wires. Because of this slightly greater irregularity in the potential differences of the unshorted electrodes, we shorted ours throughout most of our determinations.

It is interesting to note that when the electrodes are prepared and cleaned in this way they seem to take up fairly well defined potential differences which appear to be characteristic of the metal comprising the electrodes. For instance, in Series A, electrodes Nos. 1 and 2 could always be counted on to give an equilibrium potential of something less than 0.000010 volt, while electrodes Nos. 3 and 4 gave equilibrium potentials between 0.000010 and 0.000020 volt and Nos. 5 and 6 a value of about 0.000010 volt. These characteristic values reappeared time and time again throughout several years whenever these electrodes were coupled, although the electrodes were remade during that time, in some cases a number of times, and cleaned and used many times.

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[12] Morgan and Lammert, THIS JOURNAL, 45, 1692 (1923).

[13] Travers, "Thesis," Vassar College, 1928.

To see whether this method of cleaning and drying gave results of the same order of magnitude as those obtained when the electrodes were heated, we heated a number of electrodes, selecting electrodes whose characteristic behavior was well known to us because of a large number of results available. Of the seventy-eight electrodes heated, nine cracked and gave the abnormally large results characteristic of cracked electrodes. Furthermore there was very little gain in precision when the electrodes were heated. The average potential, the range of differences and the deviations are practically the same. With the gold electrodes, however, the results were more satisfactory although the tendency of the gold electrodes to crack was greater. However, whereas the air-dried electrodes are likely to give higher initial readings, which then drop to a constant potential difference if the electrodes are short circuited, the flame heated electrodes are likely to give lower initial readings which then rise to higher values in the course of an hour. All in all there seems to be little advantage in the method of heating the electrodes over the method of air drying them and considerable disadvantage due to the readiness with which they crack.

A few determinations on the reproducibility were obtained when the electrode was not dried but was rinsed with some of the acid solution used. Our experience with conductance cells led us to believe that there would be no difficulty in obtaining at least as satisfactory a reproducibility as could be obtained with the dried electrodes but our results indicate that while the gold wires are if anything more readily reproducible with this method, the platinum electrodes are not, the averages, ranges and deviations all being higher when the electrodes are only rinsed. We varied the treatment somewhat, rinsing the electrodes one time with 0.1 *N* hydrochloric acid immediately after distilled water, another time with alcohol before the 0.1 N hydrochloric acid and still another time with alcohol and 0.1 N hydrochloric acid which was saturated with quinhydrone, but observed no striking difference in the results by different methods. Moreover, inasmuch as the quinhydrone electrode has many applications in solutions which are likely to be limited in amount, the results with the dried electrodes are the more valuable and interesting.

The Preparation of the Quinhydrone Solution.—The influence of the method of preparation of the quinhydrone and subsequent purity on the potentials of quinhydrone electrodes have been the subject of a number of investigations, reference to which is omitted in the interests of brevity. These investigations indicate very generally that the purity of the quinhydrone is of little importance in its effect upon the potential in so far as traces of iron and similar foreign substances are concerned but that methods of preparation and of drying involving raised temperatures or any other procedure which in any way alters the equimolecular proportion of quinone and hydroquinone are to be avoided. Inasmuch as the Eastman product had been compared with other preparations by a number of investigators and inasmuch as we were interested only in the reproducibility of the electrode we used the quinhydrone furnished by the Eastman Kodak Company without further purification. Moreover, we found no difference in the potentials obtained with different lots of quinhydrone, all of which came from the same company.

The concentration of quinhydrone to be used in solution has also been the subject of investigation, the work done indicating that in accordance with the theory of the electrode the concentration of quinhydrone exerts very little influence on the potentials obtained if the concentration is not too low. Biilmann and Jensen[8] have made perhaps the most conclusive study of this point and find that the potentials of cells made up 0.00320 *M* or more concentrated in quinhydrone agree very well with the potentials of cells prepared by saturating the solutions with quinhydrone. However, since the solutions are so readily saturated with quinhydrone we used the saturated solutions throughout the investigation. At the end of each experiment some of the excess quinhydrone remained undissolved. No difference in result was obtained when the quantity of quinhydrone was increased or decreased nor when the solution was heated slightly above 25°. However, whenever the solutions were heated to a temperature above 50°, the potential differences were larger and the solution became dark colored in a much shorter time. For this reason we did not heat the solutions before immersing the electrodes.

We made a number of determinations to discover whether there was any difference in the potential differences obtained when the solutions were stirred and when they were not stirred. We found that the average potential difference, range and deviations are of about the same magnitude, but that in the case of measurements in the unstirred solutions the potential differences varied about a mean value rather than approached an equilibrium value. Therefore, to obviate one source of variation, we stirred our solutions throughout most of our work and recommend that this be done whenever feasible, although it is recognized that to do this would frequently complicate the technique in a given application and would be impossible in others.

The Size and Composition of the Metal Electrode.—Our results on the effect of size and composition of the metal electrode on the reproducibility of the quinhydrone half-cells are summarized in Tables I and II. The voltages given are the average of a number of values taken after the electrodes had been immersed in the solution for at least an hour. The values which are averaged for the short-circuited electrodes represent the potential differences between pairs of electrodes which had been connected during cleaning and between one electrode of the series taken as a reference and the other members of the series, one by one. Our reason for taking the averages of values after sixty minutes is that in our experience any electrodes which, under the conditions of our experiments, will come to equilibrium eventually have done so by that time, which is to say successive readings agreed with one another to within at least 0.000005 volt. To report only the equilibrium values, however, is to exclude many of the results obtained with the small wires and to do this gives an impression that the results with the small wires are better than they are in reality. These results are typical of a larger number of results obtained in the early part of this work before all of the refinements of technique had been developed. In a few cases, however, several results, which were so entirely inconsistent with the rest of the series that they appeared as accidental errors, were discarded, but when this was done the number discarded is indicated in the last column of the table and the original range indicated in parentheses beneath the other value.

TABLE I

COMPARISON OF THE POTENTIAL DIFFERENCES OBTAINED AFTER SIXTY MINUTES IN 0.1000 *N* HYDROCHLORIC ACID SOLUTION SATURATED WITH QUINHYDRONE BETWEEN ELECTRODES MADE OF METALS OF DIFFERENT DIMENSIONS AND COMPOSITIONS WITH DIFFERENT PRETREATMENT METHODS; SOLUTIONS STIRRED

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying opns. between meas.	Av. potential difference, volt	Ranges of diff., 0.000000 to − (volt)	Av. deviation, mv.	Number results discarded in average
Small Wires							
Shorted Pt, 7–12	6	76	4	0.000008	0.000025 (.000087)	0.005	3
Shorted O, 1–6	6	101	6	.000016	.000041	.008	0
Unshorted O, 1–6	6	39	2	.000024	.000067	.015	0
Shorted **Au.** 7–12	6	76	4	.000066	.000330 (.000640)	.075	1
Shorted Ir, 7–12	6	40	2	.000009	.000027	.005	0
Shorted Rh, 7–12	6	22	2	.000011	.000020	.004	0
Large Wires							
Shorted **A,** 1–6	6	94	5	.000009	.000026	.005	0
Unshorted **A,** 1–6	6	51	3	.000008	.000022	.004	0
Shorted B, 1-6	6	120	6	.000004	.000025	.003	0
Unshorted B, 1-6	6	53	3	.000010	.000042 (.000054)	.009	1
Shorted Pt, 1-6	6	150	9	.000012	.000042 (.000088)	.007	2
Unshorted Pt, 1-6	6	50	3	.000011	.000037 (.000069)	.007	2
Shorted **Au,** 1–6	6	132	7	.000013	.000058	.011	0
Unshorted **Au,** 1–6	6	36	2	.000010	.000025 (.000072)	.004	2

TABLE I (*Concluded*)

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying opns. between meas.	Av. potential difference, volt	Ranges of diff., 0.000000 to —(volt)	Av. deviation, mv.	Number results discarded in average
Shorted Ir, 1-6	6	84	6	0.000011	0.000034 (.000057)	0.006	2
Unshorted Ir, 1–6	6	44	2	.000006	.000024	.004	0
Shorted Rh, 1-6	6	86	6	.000005	.000014	.005	0
Unshorted Rh, 1-6	6	41	2	.000006	.000028	.004	0
Shorted St, 1-6	6	106	6	.000007	.000024 (.000064)	.004	1
Unshorted St, 1–6	6	41	2	.000007	.000020	006	0
Special Wires							
Shorted **Am.** Pt, 1–6	6	74	4	.000014	.000053	.008	0
Unshorted **Am.** Pt, 1-6	6	39	2	.000012	.000027	.006	0
Shorted L. & N., 1-4	4	42	4	.000002	.000008	.002	0
Foils							
Shorted P_{11-1}-P_{11-4}	4	54	4	.000004	.000018	.003	0
Unshorted P_{11-1}-P_{11-4}	4	21	2	.000003	.000010	.003	0
Shorted G_{11-1}-G_{11-4}	4	51	4	.000006	.000019 (.000064)	.003	1
Unshorted G_{11-1}-G_{11-4}	4	15	2	.000002	.000007 (.000250)	.002	3
Shorted P_{12-1}-P_{12-4}	4	54	5	.000004	.000009	.002	0
Unshorted P_{12-1}-P_{12-4}	4	28	3	.000004	.000010	.003	0
Shorted D-F	6	85	5	.000004	.000015	.003	0
Unshorted D-F	4	9	1	.000002	.000005	.002	0
Shorted G_{12-1}-G_{12-4}	4	47	5	.000004	.000013	.003	0
Unshorted G_{12-1}-G_{12-4}	4	25	3	.000003	.000013 (.000055)	.003	4
Shorted P_{13-1}-P_{13-4}	4	40	3	.000004	.000009	.003	0
Unshorted P_{13-1}-P_{13-4}	4	23	2	.000004	.000009 (.000019)	.003	1
Shorted G_{13-1}-G_{13-4}	4	50	5	.000004	.000015 (.000022)	.003	2
Unshorted G_{13-1}-G_{13-4}	4	20	2	.000008	.000030 (.000039)	.006	1
Shorted P_{22-1}-P_{22-4}	4	63	6	.000003	.000011	.002	0
Unshorted P_{22-1}-P_{22-4}	4	26	2	.000002	.000008	.002	0
Shorted I-N	6	50	4	.000003	.000008 (.000016)	.002	2
Shorted G_{22-1}-G_{22-4}	4	53	6	.000004	.000011 (.000020)	.002	1
Unshorted G_{22-1}-G_{22-4}	4	26	2	.000009	.000026	.008	0
Shorted P_{23-1}-P_{23-4}	4	56	6	.000003	.000009	.002	0
Shorted G_{23-1}-G_{23-2}	2	8	3	.000007	.000012	.002	0

From these results it is obvious that the size of the metal electrode has a very definite effect upon the reproducibility possible with the quinhydrone

TABLE II

SUMMARY OF RESULTS SHOWING THE PERCENTAGE VARIATION IN POTENTIAL DIFFERENCES OBTAINED WHEN METALS OF DIFFERENT COMPOSITIONS AND DIMENSIONS ARE USED IN THE PREPARATION OF THE QUINHYDRONE ELECTRODE. SOLUTIONS STIRRED

Electrode	Total number measured	Percentage of total <0.000010 volt	<0.000050 volt	<0.000100 volt	>0.000100 volt
Small Wires					
O, 1-6	140	27	96	100	0
Pt, 7–12	79	53	99	100	0
Ir, 7–12	40	68	100	100	0
Rh, 7–12	22	32	100	100	0
Au, 7–12	77	27	62	79	21
Large Wires					
A, 1–6	145	56	100	100	0
B, 1–6	174	82	99	100	0
Pt, 1–6	204	50	98	100	0
Ir, 1–6	130	55	98	100	0
Rh, 1–6	127	85	100	100	0
Au, 1–6	170	58	96	100	0
St, 1-6	148	72	99	100	0
Special Wires					
Am **Pt,** 1–6	113	40	99	100	0
L. & N., 14	42	100	100	100	0
Foils					
P_{11-1}-P_{11-4}	75	92	100	100	0
G_{11-1}-G_{11-4}	70	83	96	97	3
D-F	94	94	100	100	0
P_{12-1}-P_{12-4}	82	96	100	100	0
G_{12-1}-G_{12-4}	76	87	99	100	0
P_{13-1}-P_{13-4}	64	98	100	100	0
G_{13-1}-G_{13-4}	73	84	100	100	0
I-N	62	96	100	100	0
P_{22-1}-P_{22-4}	89	98	100	100	0
G_{22-1}-G_{22-4}	80	85	100	100	0
P_{23-1}-P_{23-4}	56	100	100	100	0
G_{23-1}-G_{23-2}	8	75	100	100	0

electrode in 0.1 hydrochloric acid. Both the average potential differences and the range of differences are greater as the size of the electrodes decreases; the larger electrodes reach a constant equilibrium value more readily than the smaller electrodes. Moreover, with the smaller wires, and particularly with the smallest gold wires, the range on the bridge wire over which there is no deflection on the galvanometer becomes greater and the results more erratic. Frequently no equilibrium value is obtained.

This would seem to indicate that when cells are made of such **very** small wires the capacity of the cell is so low that, even with the potentiometer method, enough current is drawn from the cell, while determining the null point, to destroy the equilibrium and hence make the voltage vary. It is probably variations such as these, coupled with additional variations due to concentration polarization, which made it impossible for Biilmann and Lund[14] to use their capillary electrode for more than one or two readings; the question naturally arises where such small electrodes are employed, as to what may be the accuracy of these initial readings. It is possible that a more fortunate form of the microelectrode would be of a type suggested by Boëz[15] in which a sheet of platinum in contact with quinhydrone and two or three drops of the liquid to be examined is held between two cover glasses, since in this type a larger surface of metal could be used.

Table I also gives data on the effect of the composition of the metal on the reproducibility of the quinhydrone electrode,

Upon no point in connection with the quinhydrone electrode has there been such lack of agreement among different investigators as upon the composition of the metal to be used. One group of investigators prefers gold or gold plate, Corran and Lewis[16] suggested that platinum may act as a catalyst for the oxidation of quinol; another group prefers platinum; and still another group reports equally successful reproducibility of potential for either gold or platinum.

Biilmann[g] states that platinum which has been dulled by use should be avoided and that only new bright platinum should be employed, that platinum is preferable to gold for experiments of minute accuracy, since concentrations of quinhydrone sufficient to give exact potentials with bare platinum are not sufficient with gold but that there are some systems in which platinum may not be used.

Any comparison of our results with those of earlier investigators is extremely difficult, since in the first place, while a number of investigators state a preference, they do not always give data to substantiate their preferences, with the result that we do not know even the order of the precision which they are describing. In the second place, the size of the metal is frequently not stated and size is a factor which we find of greater importance than the composition of the electrode. It is quite probable that the entire issue is confused by the fact that some investigators are drawing conclusions as to the precision of the quinhydrone electrode in certain complex systems when they are using electrodes which are too small to give precise results in any systems.

However, in so far as measurements in 0.1 N hydrochloric acid are typical, our results indicate that if an electrode larger than one square centi-

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[14] Biilmann and Lund, Ann. *chim.*, [9] 16, 321 (1921).

[15] Boëz, *Compt.* rend. *soc.* biol., 101, 524 (1929).

[16] Corran and Lewis, Biochem. J., 18, 1358 (1924).

meter is used, different pieces of the same sample of metal give potential differences, when used as quinhydrone electrodes, which are reproducible with great precision. Table II indicates that it is extremely probable that two pieces of foil larger than one square centimeter of any composition will give potential differences, when cleaned in cleaning mixture, rinsed in water and dried in air, and measured in a solution containing dissolved air under a pressure of one atmosphere, which agree with one another to within something less than 0.00001 volt. This is true whether the metal is the purest gold or platinum obtainable and quite new or whether it is platinum whose exact composition is unknown and which is so old, dulled, roughened and battered (Series D-F and I-N) that it can scarcely be recognized. It is true that we had a few more inexplicably and quite suddenly high results with the gold foils than with the others; on the other hand, the large-surface gold electrodes (L. & N. Nos. 1–4) which we purchased from Leeds and Northrup at two different times gave us some of the best results we had. Quite contrary to Biilmann's experience we found the old platinum foils as good as if not preferable to the new.

As the size of the metal surface diminished, however, we found certain differences in reproducibility among the different metals. The old platinum gave lower averages, ranges and deviations and incidentally reproduced these same results very consistently time after time. The iridium and rhodium alloyed platinum (Series Ir Nos. 1–6, 7–12 and Rh Nos. 1–6, 7–12) gave results which indicated that the reproducibility of different pieces of these metals was of the same order as that of pure platinum (Pt Nos. 1–6, 7–12) purchased at the same time except for the larger rhodium alloyed wires, which gave results lower than either the iridium alloy or pure platinum. Furthermore, all of these electrodes improved in reproducibility as they were used. The old platinum wires (Series A Nos. 1–6 and B Nos. 1–6) gave lower averages, etc., than any of the newer metals except the rhodium alloy. The C. P. platinum from the American Platinum Company recommended by Cullen (Am. Pt Nos. 1–6) gave results intermediate between the results obtained with two samples of platinum from other companies (Pt Nos. 7–12, O Nos. 1–6) which were also smaller in diameter. These electrodes also improved with use. The largest gold wires (St Nos. 1–6), like the foils, gave results as reproducible as the other metals, but the next size of wires (Au Nos. 1–6) and particularly the smallest wires (Au Nos. 7–12) gave much larger values. In fact, *so* troublesome were the very small wires that time and time again we examined the electrodes for cracks, only to find no evidence of any faulty construction whatsoever.

In conclusion, then, we recommend that, from the point of view of the reproducibility of different pieces of the same sample of metal when used for the quinhydrone electrode in 0.1 *N* hydrochloric acid in the presence of air, pieces of platinum foil, preferably old and roughened, of at least one square centimeter surface be sealed into soft glass tubing in the usual manner with sealing-in glass and carefully annealed; further, that electrodes so made be tested for leaks, by boiling in hot water, and cleaned, after the tubes are filled with mercury, by immersion in cold chromic acid cleaning mixture prepared from C. P. chemicals, which is then heated to about 125° and slowly cooled, the electrodes being short-circuited in pairs. The electrodes then should be carefully rinsed in distilled water and in alcohol and dried for about twenty minutes in a current of purified air, after which they should be immersed in the solution whose hydrogen-ion concentration is to be measured, to which has been added quinhydrone in excess of the solubility (0.4–0.6 g. per 100 cc. of 0.1 *N* hydrochloric acid). Several electrodes should be immersed for a preliminary intercomparison to eliminate the possibility of a cracked electrode being used. More consistent results are obtained if the solution can be stirred. Gold foils may be substituted for platinum foils but they are more troublesome to work with, since the metal is softer, give erratic results if accidentally contaminated with mercury, and must be welded to platinum wires to be sealed into glass.

Electrodes prepared in this way give results of great precision with ease and a reproducibility which in our experience is far more satisfactory than that possible with any of the other standard electrodes.

We are indebted to the Special Research Fund of Columhia University for a grant for this work, without which it could not have been completed.

Summary

A study has been made of the reproducibility of the quinhydrone electrode in 0.1 *N* hydrochloric acid under varying conditions and with a large number of electrodes of different sizes, ages and compositions, from which study the following conclusions may be drawn.

1. The quinhydrone electrode can be reproduced with ease and with great precision, two electrodes made from the same piece of foil consistently giving potential differences agreeing with one another to less than 0.000010 volt.

2. The greatest source of error in the quinhydrone half-cell lies in the preparation of the metal electrode, differences of almost 0.1 volt having been observed when the glass of one of the electrodes was cracked. For this reason a method of making, testing and cleansing the electrodes, which reduces the breakage to a minimum, is suggested.

3. The results which are obtained when the electrodes are heated in an alcohol flame before use do not justify the method in view of the large number of electrodes which crack.

4. Electrodes made of longer pieces of wire which can be connected directly to the potentiometer wires without the use of mercury as a con-

necting medium do not give any better results than electrodes made of short wires.

5. The size of the metal exposed to the solution determines the precision with which electrodes properly prepared may be reproduced. Very small, short wires give erratic results, larger, short wires give consistent results but larger deviations than foils or longer lengths of wire, but two foils with dimensions greater than one square centimeter give differences of potential, when measured against one another, of less than 0.000010 volt.

6. The cumposition and age of the metal comprising the electrode is of little importance if the electrode is large enough. However, in 0.1 *N* hydrochloric acid when the electrodes were much smaller than one square centimeter, old roughened platinum seemed to give better results than either new platinum, platinum alloyed with iridium or gold, but the platinum and platinum alloys gave better results than the gold.

Two pieces of metal, cleaned and dried by the method suggested give very nearly the same potential differences whenever they are measured against one another, which fact enables an investigator to select, from a group of electrodes, a few electrodes whose potential differences will invariably be reproduced with great precision.

Work on the effect of nitrogen and on the reproducibility and accuracy of the electrode under other conditions is in progress.

NEW YORK, N. Y.
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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 273]

REDUCTION POTENTIAL OF QUADRIVALENT TO TRIVALENT IRIDIUM IN HYDROCHLORIC ACID SOLUTION

BY SHO-CHOW WOO

RECEIVED NOVEMBER 10, 1930 PUBLISHED FEBRUARY 9, 1931

Introduction

It is well known that the most stable compounds of iridium in hydrochloric acid solution are the ions of hexachloriridic and hexachloriridous acids, H_2IrCl_6 and H_3IrCl_6, in which the iridium is present in the quadrivalent and the trivalent states, respectively. Earlier investigations of these compounds were restricted to the determination of their formulas, and until very recently no studies had been made to determine their physico-chemical properties. Since this research was undertaken, however, Ogawa[1] has published measurements of the electromotive force of cells in which the sodium salts of the chloriridic and chloriridous acids were used. He observed steady changes in the electromotive force, and

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[1] E. Ogawa, *J. Chem. Soc. Japan*, **50**, 123 (1929).

attributed this to the hydrolysis of the salts in the absence of any added acid. In view of the inconstancy of his results it seems desirable to present the determinations that have been made in this Laboratory of the reduction potential for the combination quadrivalent–trivalent iridium in hydrochloric acid solution.

The value of this potential was derived from measurements of the electromotive force of the cell

$$\mathrm{Ir},\ \left\{\begin{matrix}\mathrm{IrCl_6^{=}}\ (c_1\ f.)\\ \mathrm{IrCl_6^{\equiv}}\ (c_2\ f.)\end{matrix}\right. + \mathrm{HCl}\ (1\ f.)\Big\}.\ \mathrm{HCl}\ (1\ f.),\ \mathrm{H_2}\ (p\ \mathrm{atm.}),\ \mathrm{Pt}$$

The methods of. preparation of the iridium solutions and the analytical procedures employed will be described in a later article.

This research was suggested by Professor A. A. Noyes, and to him and to Professor Don M. Yost the author is indebted for many helpful suggestions.

Procedure for the Electromotive Force Measurements.—The type of electrode vessel used was that commonly employed in this Laboratory.[2] The hydrogen was prepared by electrolyzing a solution of sodium hydroxide between nickel electrodes, and it was freed from oxygen by passing it over a glowing tungsten spiral. Before entering the cell, the gas passed through a hydrochloric acid solution of the same concentration as that in the cell.

In order to reduce the liquid potential to a very low value, the concentration of the hydrochloric acid in the iridium solutions was made the same as that used in the hydrogen half-cell, and the total concentration of iridium was made small.

The concentration of the hydrochloric acid in the iridium stock solutions was determined by titrating them with sodium hydroxide, using phenolphthalein as an indicator, after the quadrivalent compound had been reduced to the trivalent state with pure silver. The desired acid concentration for the cell solutions was attained by diluting the stock solutions with the proper amount of hydrochloric acid of known strength. The two half-cells were separated by an ungreased stopcock which was moistened with the acid but was kept closed.

It was found that gold and platinum (to a much less extent) were attacked by the chloriridic acid, but that iridium was not so attacked as was shown by the constancy of the potentials and concentrations. This fact resulted in the use of an iridium-plated glass tube as the electrode in the iridium half-cell. When nitrogen was bubbled through the iridium solution for the purpose of stirring it, the potential did not attain a constant value but usually decreased steadily. With a mechanical stirrer, however, the final electromotive force was reached in a few hours and then remained constant over long periods. The nitrogen may have

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[2] Schuhmann, THIS JOURNAL, 46, 52 (1924).

contained some oxidizable impurity, for the concentration of the quadrivalent iridium was found to be always less (even 30–40% less) at the end of an experiment than at the beginning. No concentration changes were observed when the mechanical stirrer was used.

Results of **the** Electromotive Force Measurements.-—In Table I is given a summary of the observed values of the electromotive force. The total acid concentration was always 0.998 *f.* (hereafter regarded as 1.0 f.). The "corrected electromotive forces given in the last column are the values of the electromotive force calculated by the usual logarithmic formula for the case that the pressure of hydrogen is one atmosphere and the concentrations of the two forms of iridium are equal. The given electromotive forces, expressed in volts, are those of the cell in the direction in which it was written above.

TABLE 1

RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS

Cell	Temp., °C.	Formal concentration $IrCl_6^-$	Formal concentration $IrCl_6^=$	Pressure of hydrogen	Electromotive force Observed	Electromotive force Corrected
1	25	0.004864	0.005163	719.5	−1.02403	−1.0263
2	25	.004838	.005189	720.2	−1.02365	−1.0261
3	25	,002477	,007631	719 7	−0.99689	−1.0265
4	25	.001976	.008148	720.1	− .98910	−1.0262
5	25	.001976	,008148	719.7	− .98953	−1.0267
					Mean	−1.0264
6	25			721.6	−1.02355	−1.0264
	20			719.8	−1.02840	−1.0313
7	25			721.7	−1.02243	−1.0264
	20			720.7	−1.02735	−1.0313

Discussion of the **Results**

The constancy of the corrected electromotive forces in Cells 1–5 shows that the ratio of the activity coefficients of the chloriridate ion and chloriridite ion does not change appreciably with change in their relative concentrations within the limits here involved. This behavior was to be expected since the difference in the ionic strengths of the solutions is small. Mention should be made, however, of the fact that less satisfactory corrected values were obtained with cells in which a large excess of the chloriridate was present. No explanation of this fact could be found. The difference, however, did not exceed 10 millivolts.

The mean value of the electromotive force at 25° is −1.0264 volts for the cell

$$\text{M, } IrCl_6^= \ (cf.) + IrCl_6^- \ (cf.) + HCl \ (1.0 f.), HCl \ (1.0 f.), H_2 \ (1 \text{ atm.})$$

By taking the mean activity coefficient of the ions in 1.0 f. HCl to be 0.823 as given by Lewis and Randall[3] and assuming that the H^+ and Cl^-

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[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923,** p. 336.

ions have in this acid equal activities, this electromotive force may be referred to the molal hydrogen electrode, in which case it becomes —1.021 volts. This is the value for the hypothetical cell

$$\text{M}, \text{IrCl}_6^{\equiv}(c\text{ f.}) + \text{IrCl}_6^{=}(c\text{f.}) + \text{HCl}\ (1.0\text{ f.})\ \text{H}^+\ (1\ m.), \text{H}_2\ (1\text{ atm.})$$

Under the usual conventions[4] this value is also the molal electrode potential for the electronic reaction

$$\text{IrCl}_6^{\equiv}\ (c\,f.) = \text{IrCl}_6^{=}\ (c\text{f.}) + \text{E}^-\ (1\text{f.})\ \text{in } 1.0\,f.\ \text{HCl at } 25°$$

In all these cases c is understood to have a value between 0.002 and 0.008 molal.

This potential corresponds to a greater reducing power than the value (—1.369 volts) for the chlorine electrode. It shows that chloriridous acid is oxidized to cltloridic acid by chlorine at atmospheric pressure so completely that the unoxidized portion is entirely inappreciable.

The corresponding value of the free energy decrease attending the reaction

$$\text{IrCl}_6^{\equiv}\ (c\text{f. in } 1.0\text{ f. HCl}) + \text{H}^+\ (1\text{ m.}) = \text{IrCl}_6^{=}\ (c\text{f. in } 1.0\ f.\ \text{HCl}) + {}^1/_2\,\text{H}_2\ (1\text{ atm.})$$

or attending the above formulated electronic reaction (under the convention that the free energy change H^+ at 1 m. $+ \text{E}^- = {}^1/_2\text{H}_2$ at 1 atm. is zero), is **—23,540** cal. at 25°.

From the measurements of the electromotive force of cells 6 and 7 at 25 and at 20° the value +0.00098 volt/degree is obtained for the temperature coefficient $d\text{E}/d\text{T}$; and from this the corresponding value of the heat content increase ΔH attending this last reaction is found to be **+30,400** cal.

Summary

There have been here presented measurements which show that half-cells consisting of metallic iridium in contact with a 1.0 formal hydrochloric acid solution of equimolal quantities of chloriridic and chloriridous acids (H_2IrCl_6 and H_3IrCl_6) at a concentration (c) between 0.002 and 0.008 formal, when measured against a half-cell consisting of a platinum electrode in contact with hydrogen gas at one atmosphere and with 1.0 formal hydrochloric acid solution, have an electromotive force of **—1.0264** volts at 25°, and of **—1.0313** volts at 20°. Referred to the molal hydrogen electrode (H^+ with activity 1.0 molal), the value of the reduction potential at 25° is computed to be —1.022 volts for the reaction

$$\text{IrCl}_6^{\equiv}(c\ f.\ \text{in } 1.0\text{ f. HCl}) = \text{IrCl}_6^{=}\ (c\text{f. in } 1.0\text{ f. HCl}) + \text{E}^-\ (1\text{f.})$$

The corresponding value of the free energy decrease is **—23,540** calories. From the temperature coefficient of the electromotive force, the heat content decrease for this electronic reaction is found to be **—30,400** cal.

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[4] See Noyes and Sherrill, "Chemical Principles," The Macmillan Co., New York, 1922, pp. 255–258.

[CONTRIBUTION NO. 647 OF THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

SOLUBILITY OF THALLOUS IODATE IN ETHYL ALCOHOL–WATER MIXTURES

BY VICTOR K. LA MER AND FREDERICK H. GOLDMAN

RECEIVED NOVEMBER 14, 1930 PUBLISHED FEBRUARY 9, 1931

In two important papers Scatchard[1,2] has shown that the simple electrostatic formula first given by Born for the electrical work of transferring charged spheres of average radius r from a medium of dielectric D_1 to one of dielectric D_2, namely,

$$\log_{10} \frac{S_1}{S_2} = \frac{0.4343}{2r} \frac{\epsilon^2}{kT} \left(\frac{1}{D_2} - \frac{1}{D_1}\right)$$

accounts for the solubility data on sodium chloride and potassium chloride in ethyl alcohol–water mixtures over the entire composition range by using such plausible values as $r = 1.31$ and 1.35 Å. He was careful to remark, however, that this simplified theory works better than one has any right to expect.

In connection with our solubility studies[3] on thallous iodate in aqueous salt solutions, we have tested whether this formula would also apply to thallous iodate—alcohol–water mixtures. This salt has the obvious advantage that its solubility is so small that the correction for interionic attraction is negligible in the absence of added salts. The Debye–Hückel limiting law is adequate[4] to correct for this effect if desired. The ease with which iodates may be determined enables determinations of the solubility to be made with sufficient precision when considerable alcohol is present.

Experimental

The preparation of the salt and method of analysis have been described in detail previously.[3] The ethyl alcohol was redistilled from caustic potash and silver nitrate and the solvents made up by weight. Density measurements were made in each case as a check on the accuracy of this procedure.

Discussion

The data are tabulated in Table I, the solubility being expressed in micro (10^{-6}) moles per liter. Column 6 shows that log $S_{H_2O}/S_{\text{alcohol}}$, when divided by the mole fraction, drifts steadily downward by 22%. On the other hand, Column 7 shows that log $S_{H_2O}/S_{\text{alc.}}$ is an almost linear function (to within 7%) of the weight percentage of alcohol over the same concentration range. In Column 8 we give $(-\log f_0)$, the correction for interionic attraction in each solvent employed in calculating Column 9. The linear relation in respect to weight percentage is unaltered.

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[1] Scatchard, THIS JOURNAL, 47, 2098 (1925).

[2] Scatchard, *Chem. Rev.*, 3, 383 (1927).

[3] La Mer and Goldman, THIS JOURNAL, 51, 2632 (1929).

[4] Ref. 3, p. 2640, Fig. 2.

TABLE I

SOLUBILITIES OF THALLOUS IODATE IN ETHYL ALCOHOL–WATER MIXTURES AT 25°

Wt. % alcohol	Soly. · 10^6 mole/liter	Density measured	N Mole fraction alcohol	Log $\frac{S_{H_2O}}{S_{alc.}}$	$\frac{\text{Log} \frac{S_{H_2O}}{S_{alc.}}}{N}$	$\frac{\text{Log} \frac{S_{H_2O}}{S_{alc.}}}{\text{Wt. \%}}$	$-\log f_0$	$\frac{-\log f}{\text{Wt. \%}}$
0.00	1841	0.99708	0.0000	0.0000	..	....	0.0217	
4.25	1416	.9894	.01706	.1140	6.68	0.0268	.0204	0.0264
11.56	914.7	.9780	.0488	.3037	6.21	.0263	.018	.0260
21.37	503.8	.9644	.0960	.5627	5.86	.0263	.016	.0262
31.61	297.1	.9478	.1530	.7921	5.17	.0251	.014	.0249
40.51	134.5	.9304	.2105	1.1363	5.39	.0280	.011	.0277
46.91	83.2	.9167	.2569	1.3449	5.24	.0287	.013	.0285
94.71	Solubility too small to be detected.							

It is unfortunate that Nernst's[6] measurements on the dielectric constants of alcohol–water mixtures do not extend below about 46 weight per cent., so that we might compare the solubility changes with the concentration dependence of $1/D$ without resorting to interpolation over the interval 0 to 46% alcohol. If Equation 1 is to hold, $1/D$ must be more nearly proportional to the weight concentration than to the mole fraction in this range of concentration. This question should be investigated with more modern experimental methods.

If we substitute in Equation 1 for D_1 and D_2, the values 78.8 (H_2O) and 49.6 (46.91% alcohol) and for S_1 and S_2 the solubility of thallous iodate in moles per liter, we compute $r = 0.78$ Å. The volume molar scale has been used in this connection by most investigators but it implies that if there were no electrical effects, the molar solubility would be constant in all solvents. There is no adequate justification for such an ideal law. If we assume Raoult's law to be the ideal, which law demands that the components in the liquid state mix in all proportions without change of volume or of heat content, then the solubility in terms of mole fraction should be identical in the absence of electrical or other effects.

Although volume no longer appears explicitly in this ideal law, the choice of molecular weights for the components used in calculating the mole fraction implies it through the Avogadro hypothesis. Assuming the molecular weights of alcohol and water to be 46 and 18.02, respectively, we get $N_1 = 33.26\cdot10^{-6}$ and N_2 = 2.29.10–t Substituting these values for S_1 and S_2 we find $r = 0.90$ Å. as the average radii of the Tl^+ and IO_3^- ions, on the assumption that the non-ideality arises solely from the net charges on the ions and that our assumptions of the molecular weights of water and alcohol are correct for their mixtures.

Either value of r, namely, 0.78 or 0.90 Å., is a trifle smaller than one might expect for the average radii from other methods of measurement. On the other hand, it actually proves to be as large as the parameter "*a*,"

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[5] Nernst, *Z. physik. Chem.*, 14,622 (1894).

representing the distance of closest approach of the ions computed with the aid of the general solution of the Debye–Hückel interaction theory.[6] If the ions are spherical and no forces of deformation intrude, "*a*" should equal 2r.

Table II gives the results of computations based upon the solubility data in dilute salt solutions. In the case of uni-univalent solvent salts the calculations can be made with fewer mathematical complications than is the case with higher valence solvent salts.

TABLE II

CALCULATION OF "*a*" ROR THALLOUS IODATE RROM ACTIVITY COEFFICIENTS OBTAINED BY SOLUBILITY METHOD. "*a*" IN Å. UNITS (DATA BY LA MER AND GOLDMAN, REF 3, PAGE 2639)

Solvent	κ	$-\log f$	"a_{1st}"	"$a_{g.}$"
0.05 *M* KNO_3	0.07505	0.1120	+O. 39	+1.57
.10 M KNO_3	,10512	.1525	+ .56	+1 50
.30 *M* KNO_3	.18073	.2509	+ .59	+ 1 31
.10 M $NaNO_3$	.10512	.1514	+ 64	t1.55
.05 M KC1	,07512	.1242	– .94	+1 15
.10 M KC1	.10515	.1751	– .74	+1 05
.10 M NaCl	.10515	.1742	– .69	+1 10

Column 4 gives the value of "a" computed from the first or Debye approximation on the customary assumption that all individual "*a*" values in the ternary mixture: water, $TlIO_3$, and 1,-1 solvent salt, are equal. By the use of a graphical plot representing the fictitious values of "a_{1st}" which correspond to the same $-\log f$ value computed for a given "$a_{general}$" and a definite value of the Debye κ or $\sqrt{\mu}$, we can readily translate any value of "a_{1st}" into its "$a_{general}$" value. These values are given in Column **5**. No sensible error is introduced in the case of symmetrical valence types in water by considering the fifth approximation equal to the general solution if $a/Z^2 < 0.8$ Å.[7] The "a" values in the nitrate solvents are almost equal to $2r$, but the "a_g" values in the chloride solvents, although no longer absurdly negative as is the case for the "a_{1st}," are still somewhat small. In other words, the neglected higher terms in the Debye theory account for the nitrate data on a purely theoretical basis involving only one parameter but are not quite sufficient to account for the chloride data. Undoubtedly other forces leading to deformation of the ions or complex chloride ion formation occur and must be taken into account for a precise representation of the data. Similar behavior has been noted for lead iodate in 0.1 N chloride solvents.[8] We should point out, however, that a com-

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[6] Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928).

[7] The data for this conversion valid for infinite dilution have been given by La Mer, *Trans. Am. Electrochem. Soc.*, 51, 507 (1927), page 547. The conversion values for finite concentrations will be published later.

[8] La Mer and Goldman, THIS JOURNAL, 52,2791 (1930).

putation for "a" values constitutes a very critical test of the Debye–Hückel theory. The fact that the highly simplified picture employed by Debye and Hückel represents the facts for Pb^+ and Tl^+, which are known to form complexes with chloride ions at higher concentrations, as closely as it does is more remarkable than are the comparatively insignificant deviations just mentioned.

Summary

The solubility of thallous iodate has been measured in ethyl alcohol–water mixtures ranging from zero to 47% ethyl alcohol. The values of the average radii calculated using Born's formula for the electrostatic work of transfer are compared with the values of the parameter "a" computed from the interaction theory for the solubility in salt solutions as extended by Gronwall, La Mer and Sandved.

NEW YORK, NEW YORK

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COOPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES AT LOW TEMPERATURES OF MANGANESE SULFIDE, FERROUS SULFIDE AND CALCIUM SULFIDE[1]

BY C. TRAVIS ANDERSON[2]

RECEIVED NOVEMBER 17, 1930 PUBLISHED FEBRUARY 9, 1931

Pursuing its general program of study of the thermodynamic properties of metals, oxides and sulfides which are important in metallurgical processes, the Pacific Experiment Station of the U. S. Bureau of Mines has determined the heat capacities of the sulfides of manganese, iron and calcium. The thermodynamic properties of these sulfides have both theoretical interest and practical importance. The heat capacities of the oxides corresponding to these sulfides have been determined, which enables an interesting comparison to be made.[3] Knowledge of the entropies of these sulfides was especially desired for use in connection with studies of the desulfurization of iron.

The method, apparatus and accuracy have been described in previous publications,[4] but it may be noted that between the sets of experiments

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[1] This paper presents the results of work done under a cooperative agreement between the U. S. Bureau of Mines and the University of California. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Assistant physical chemist, U. S. Bureau of Mines, Pacific Experiment Station, Berkeley, Calif.

[3] Millar, THIS JOURNAL, 50, 1875 (1928); 51, 215 (1929); Parks and Kelley, *J. Phys. Chem.*, 30, 47 (1926).

[4] Anderson, THIS JOURNAL, 52, 2296, 2712 (1930).

with the different samples the thermocouple was again compared with a standard, and the standard cell checked from time to time with others having Bureau of Standards certificates.

Materials

After considerable preliminary testing of various methods of preparation of pure sulfides, the method of Schöne[5] was modified to give excellent results. Schöne passed carbon dioxide saturated with carbon disulfide vapor over heated carbonates of various metals (especially calcium), obtaining nearly quantitative yields of sulfides. It has been found that the sulfates of metals having very stable oxides are preferable to carbonates, and that control of temperature of heating, and partial vapor pressure of carbon disulfide are essential. When completeness of conversion is desired, it was also found better to prepare a number of small samples than to attempt a single large preparation. The reason for these precautions will be obvious from a consideration of the mechanism of the conversion, which probably involves the reversible formation of carbonyl sulfide from carbon dioxide and carbon disulfide.

The sample of manganese sulfide was prepared from a C. P. grade of manganese sulfate. Small portions of the sulfate were placed in a silica tube which fitted conveniently in a tube furnace. Carbon dioxide was bubbled through gas washing bottles containing carbon disulfide at 25°. The tube furnace was heated to 750°. The resulting manganese sulfide had the theoretical composition of MnS to within the limits of analytical error, in this case about 0.1%. Its density was found to be 3.93 at 21.9°. A 166.3-g. sample was studied.

The ferrous sulfide was prepared from a mixture of iron oxides which were made from strips of pure ingot iron by heating them in air for several days at about 900°. The oxide material so obtained was crushed to −14 mesh and the metallic iron separated mechanically. The iron oxides were placed in the silica tube in the combustion furnace and carbon dioxide saturated with carbon disulfide at 25° was passed over the oxide at about 850°. The resulting sulfide was definitely crystalline and had the theoretical composition of FeS to within the limits of analytical error (0.2%). It had a density of 4.65 at 23.9". The calorimeter was filled with a 270.4-g. sample.

Calcium sulfide proved to be the most difficult of the materials to prepare. Finely divided calcium sulfate was used and was placed in the silica tube which had been used for the preparation of the two other sulfides. The furnace in this case was heated to about 700° and the carbon dioxide was saturated with carbon disulfide at 27°. It was necessary to re-treat the material several times before the sulfate was completely converted to the sulfide. The resulting sulfide had the theoretical composition of CaS to within the limits of analytical error, in this case about 0.1%. The sulfide was necessarily very finely divided, since coarse material could not be completely converted. The sample was compressed into pellets at pressures of several tons per square inch, so that the calorimeter could be filled with an adequate weight of material. The pellets were broken and the calorimeter finally filled with a sample of 77.1 g. Without compressing, the contents would have been less than 10 g. The density was ***2.56*** at 23.6°.

Screen tests using Tyler screens were made on these materials and are shown in

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[5] Schöne, ***Pogg. Ann.***, 112, 194 (1861).

Table I. The sizes of the calcium sulfide, of course, do not indicate the **crystal** size, as the material was all probably finer than 300-mesh before compressing.

TABLE I

SCREEN SIZES (TYLER) OF SAMPLES

Screen size	MnS, %	FeS, %	CaS, %
+ 35	22.0	0.5	54.0
+ 48	7.0	4.5	16.5
+ 65	8.5	25.0	19.0
+100	8.0	28.5	7.0
+150	8.0	21.0	2.0
$200	11.5	14.0	1.0
−200	35.0	6.5	0.5

The **Specific Heats**

No previous low temperature measurements have been made on any of these sulfides. The results obtained in this Laboratory on the heat capacities of manganese sulfide, ferrous sulfide and calcium sulfide, expressed in gram calories (15°) per gram formula weight, are shown graphically in Fig. 1. The experimental determinations of heat capacities for ferrous sulfide and calcium sulfide are given in Tables II and III. The values for manganese sulfide, except those between 100° and 170°K. are given in Table IV. The values for the heat capacities for manganese sulfide between 100 and 170°K. with the temperature rise (AT) of the determination are given in Table V and are shown graphically in Fig. 2. Except

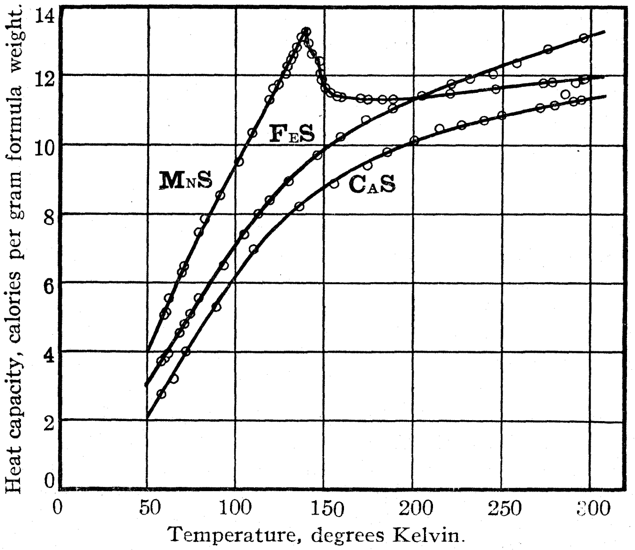

Fig. 1.—The heat capacity of manganese sulfide, ferrous sulfide and calcium sulfide in calories per gram formula weight.

for this range, the temperature rise of the determinations varied from about 3 to 6°. In changing joules to calories the factor $1/4.184$[6] was used. The calculations were made on the basis of Mn = 54.93, Fe = 55.84, Ca = 40.07, and S = 32.06.

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CALCIUM SULFIDE

T, °K	C_p	T, °K	C_p	T, °K	C_p
58.1	2.772	155.9	8.894	239.4	10.71
65.1	3.225	174.7	9.418	249.6	10.87
72.0	4.017	185.3	9.795	271.2	11.09
89.5	5.307	200.5	10.14	279.5	11.16
110.8	6.984	214.6	10.42	285.5	11.48
136.4	8.224	226.9	10.56	290.1	11.28
				294.9	11.32

TABLE III

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF FERROUS SULFIDE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
57.9	3.729	105.7	7.412	204.6	11.44
60.1	3.818	113.5	8.010	221.2	11.78
62.0	3.963	119.8	8.395	231.6	11.92
68.4	4.555	130.4	8.940	244.6	12.07
71.1	4.816	146.4	9.705	258.0	12.38
74.5	5.118	159.0	10.25	275.8	12.79
79.4	5.562	173.1	10.74	296.0.	13.12
93.7	6.512	188.2	11.07		

TABLE IV

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF MANGANESE SULFIDE

Run	T, °K.	C_p	Run	T, °K.	C_p	Run	T, °K.	C_p
1	59.8	5.068	76	187.4	11.34	89	246.0	11.64
2	62.3	5.557	77	193.1	11.38	90	257.5	11.77
3	71.0	6.485	78	199.3	11.38	91	262.8	11.79
4	79.1	7.467	79	212.9	11.50	92	268.0	11.78
5	91.8	8.529	80	216.8	11.52	93	273.0	11.80
11	291.4	11.82	81	220.5	11.51	94	278.1	11.83
34	215.3	11.43	82	218.9	11.53	95	283.4	11.88
35	60.7	5.164	83	222.7	11.55	96	289.6	11.92
36	69.9	6.296	84	226.2	11.53	97	295.3	11.92
37	82.8	7.857	85	230.3	11.54	98	175.7	11.33
73	170.1	11.36	86	232.5	11.56	99	195.9	11.39
74	174.3	11.33	87	236.0	11.58	100	204.4	11.43
75	182.4	11.32	88	239.5	11.60	101	296.9	11.93

Previous work on manganese oxide and ferrous oxide at low temperatures had shown a hump in each heat capacity curve. The ferrous oxide curve also showed a tendency at room temperature to be approaching

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[6] "International Critical Tables," Vol. I, p. 24. 4.185 abs. joules = 1 cal. = 4.1837 Int. joules.

TABLE V

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF MANGANESE SULFIDE

Run	T, °K.	AT	C_p	Run	T, °K.	AT	C_p
6	102.0	2.573	9.513	42	139.4	1.272	13.22
7	109.5	3.308	10.35	43	140.7	1.266	13.05
8	119.1	2.674	11.31	44	143.0	1.245	12.73
9	131.3	3.034	12.55	45	144.2	1.237	12.62
10	145.7	2.590	12.48	46	145.4	1.226	12.54
12	124.6	1705	11.76	47	146.7	1.213	12.53
13	128.5	1.595	12.05	48	147.9	1.230	12.08
14	1312	1.501	12.48	49	1492	1.232	11.85
15	132 8	1.457	12 62	50	150.4	1.260	11.71
16	1343	1.414	12.84	51	151.7	1.219	11.62
17	135.7	1.379	12.99	52	133.2	1.385	12 73
18	137.1	1.347	13.13	53	138.2	1.266	13.30
19	138.4	1.315	13.26	54	139.4	1.245	13.32
20	139.8	1.295	13.28	55	139.4	1.229	13.23
21	141.1	1.300	12.96	56	147.2	1.192	12.46
22	141.6	1.290	12.82	57	151.5	1.200	11.63
23	142.9	1.285	12.65	58	152.7	1.191	11.58
24	144.2	1.274	12.56	59	153.9	1.183	11.51
25	145.5	1.263	12.49	60	155.1	1.173	11.48
26	146.8	1.247	12.47	61	156.3	1.162	11.46
27	148.8	2.532	11.90	62	157.3	1.143	11.42
28	150.7	1.260	11.66	63	158.4	1.130	11.44
29	151.9	1.245	11.66	64	159.6	1.119	11.44
30	153.2	1.241	11.51	65	160.7	1.113	11.36
31	155.0	2.445	11.46	66	161.8	1.100	11.40
32	157.0	1.202	11.43	67	163.0	1.089	11.41
33	158.2	1.195	11.34	68	165.2	1.071	11.39
38	109.3	3.155	10.39	69	166.3	1.060	11.38
39	121.3	3.507	11.51	70	167.4	1.049	11.40
40	129.3	1.509	12.28	71	168.5	1.037	11.45
41	138.0	1.289	13.23	72	169.2	1.026	11.38

another anomaly. The particular sample of ferrous oxide which had been used analyzed only 83% ferrous oxide, the remaining material being a solution of iron and magnetite in the ferrous oxide.

The sample of manganous oxide was apparently a pure sample. These results would indicate that the corresponding sulfides should show anomalies at a higher temperature than their corresponding oxides. This was observed in the case of the manganese sulfide, but the ferrous sulfide curve was normal in the region where the hump was suspected. This would indicate that the hump observed in the ferrous oxide might be attributed to the solution of the magnetite and iron present in the ferrous oxide. However, the trend of the heat capacity curve for ferrous sulfide at room temperature seems to indicate that a transition is starting to take place, as in the case of the ferrous oxide. The heat capacity of the ferrous sulfide above room temperature will be measured in the near future in this Laboratory. Figure 2 shows the heat capacity curve for manganese sulfide in the vicinity of the hump, between 100 and 170°K. Just previously to Run 35 an attempt was made to supercool the manganese sulfide from room temperature to below 60°K. There was no indication of supercooling, since the points fell on the same smooth curve, independently of the history of the substance. The hump was perfectly reproducible, in fact so much so that no measurements were made on the heat of apparent transition. After reaching a maximum the downward part of the curve flattened to about 147°K., at which point it dropped off suddenly from about 12.5 to 12.0 cal. per gram formula weight. This particular anomaly seems to be more nearly a discontinuity, but was also perfectly reproducible. It was thought that this second anomaly might possibly be ascribed to the temperature scale, but after going over that portion of the scale no discrepancy could be found, indicating that this anomaly actually exists, and since the specific heat here drops almost vertically with the temperature, the correspondence with an actual discontinuity is more marked than at the maximum point. The heat capacity curve on either side of the humps possesses very different slopes, but this does not necessarily indicate a change in crystal structure, because the factors causing the anomaly are obviously active over *a* considerable temperature range and may well be affecting the normal course of the curve over a wide temperature interval. **A** study of the magnetic changes in this region would be of great interest.

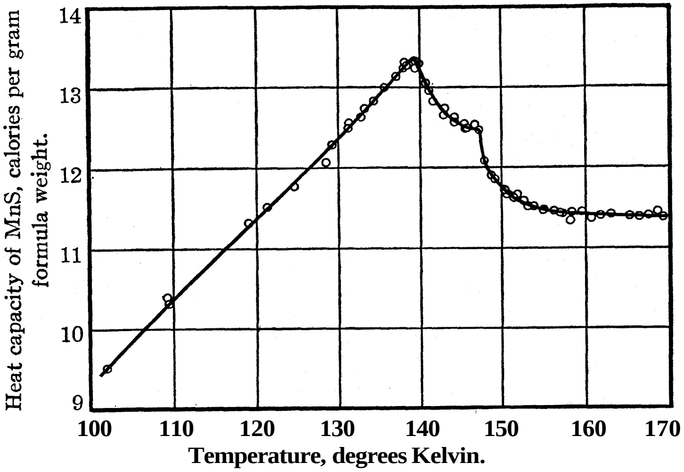

Fig. 2.—The heat capacity of manganese sulfide in calories per gram formula weight.

The experimental data on manganese sulfide do not in themselves give explanation for the double cusped nature of the hump observed. However, it is an obvious hypothesis to suppose that the curve as observed may represent the sum of two simple curves, each of which has a separate hump at temperatures near those of the cusps. This point of view has led Professor E. D. Eastman of the University of California to suggest that there may be some sort of analogy between the factors causing doublet spectral lines and those responsible for the "doublet" hump here observed.

Calculation of Entropies

The entropies were calculated graphically by plotting the heat capacity against the logarithm of the temperature. The heat capacity curves were extrapolated to the absolute zero by means of combinations of Debye and Einstein functions. The Debye functions used had the following parameters (8): for MnS, 205; FeS, 205; and CaS, 284. In Table VI are given the results of the entropy calculations.

TABLE VI

ENTROPY DATA

	MnS	FeS	CaS
Extrap. (0–56.2) °K.	2.14	1.43	1.32
Graph. (56.2–298.1) °K.	16.58	14.68	12.21
S°_{298}	18.7 ± 0.3	16.1 ± 0.3	13.5 ± 0.3

The following combinations of Debye and Einstein functions were found to fit the specific heat curves per formula weights of the three sulfides.

$$C_{\mathrm{MnS}} = D\,\frac{(205)}{T} + E\,\frac{(263)}{T}$$

$$C_{\mathrm{FeS}} = D\,\frac{(205)}{T} + E\,\frac{(370)}{T}$$

$$C_{\mathrm{CaS}} = D\,\frac{(284)}{T} + E\,\frac{(369)}{T}$$

The MnS combination fits the experimental curve up to 50°K., the FeS combination to 75° and that for the CaS to 133°.

Related Thermal Data

The heat of formation of manganese sulfide has been determined by Wologdine and Penkiewitsch[7] by direct combination of manganese and sulfur. They give $\Delta H^\circ_{298} = -62{,}900$ cal. Using this value in combination with the entropies of manganese and rhombic sulfur, as given by Lewis and Randall,[8] and the entropy of manganese sulfide given above, the free energy of manganese sulfide was calculated as —64,000 cal.

Parravano and P. de Cesaris[9] measured the heat of formation of ferrous sulfide by the combination of iron and rhombic sulfur and give $\Delta H^\circ_{298} = -23{,}070$ cal. Using their value and Lewis and Randall's values for the

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[7] Wologdine and Penkiewitsch, *Compt. rend.*, 158, 498 (1914).

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 464.

[9] Parravano and P. de Cesaris, *Gazz. chim. ital.*, *47, 144* (1917).

entropies of iron and rhombic sulfur and the measured entropy of ferrous sulfide, the value —23,600 cal. was calculated as the free energy of ferrous sulfide.

Sabatier[10] determined the heat of formation of calcium sulfide by direct union of calcium and rhombic sulfur. He gives the value of $\Delta H^\circ_{298} = -111{,}200$ cal. Using this value and the values of the entropies of calcium and rhombic sulfur as given by Lewis and Randall, and the entropy obtained for calcium sulfide, the free energy of calcium sulfide was calculated as −109,800 cal.

Summary

The heat capacities of manganese sulfide, ferrous sulfide and calcium sulfide from about 60 to 300°K. have been determined, and their corresponding entropies and free energies calculated.

The following table contains the summarized results.

	S°_{298}	ΔF°_{298}	ΔH°_{298}
MnS	18.7	–64,000	–62,900
FeS	16.1	–23,600	–23.070
CaS	13.5	−109,800	–111,200

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND THE UNIVERSITY OF OKLAHOMA]

THE DECOMPOSITION OF REFRACTORY SILICATES BY FUSED AMMONIUM FLUORIDE AND ITS APPLICATION TO THE DETERMINATION OF SILICA IN GLASS SANDS

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

RECEIVED NOVEMBER 17, 1930 PUBLISHED FEBRUARY 9, 1931

For years the opening of silicates, preparatory to the analysis of the alkali metals, has been a serious problem. The method of J. Lawrence Smith, though satisfactory as to accuracy, is laborious in technique, consequently the hydrofluoric–sulfuric acid process often has been proposed to supplant it but has been unqualifiedly rejected by Hillebrand[2] as unsuitable because of the difficulty of removing fluorides. Lundell[3] proposes to substitute perchloric acid for sulfuric to obviate this difficulty, especially with reference to soda-lime glasses. While working along the same lines, but using crystallized ammonium fluoride, the writers noticed that fusion took place and it occurred to them that possibly a molten reagent might be more ef-

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[10] Sabatier, Ann. *chim. phys.*, [5] 22, 22 (1881).

[1] Recipient of "The J. T. Baker Fellowship in Analytical Chemistry" at the University of Illinois for the year 1930–31. Assistance is further gratefully acknowledged as a result of a leave of absence granted by the University of Oklahoma.

[2] U. S. Geol. Survey Bull., 700, 99 (1919).

[3] Lundell and Knowles, J. Am. Ceramic *Soc.*, 10, 849 (1927).

fective than the aqueous solutions commonly employed. Such proved to be the case, as will be shown later.

On looking up the literature, it was found that Berzelius[4] noted the fusibility of ammonium fluoride, and that it had been employed by Jannasch[5] to decompose andalusite, but in such a way as to obscure and nullify the peculiar advantages of the reagent. For instance, the flux was formed in the reaction crucible from the aqueous reagents, ammonia and hydrofluoric acid, with the latter in large excess, necessitating the removal of at least 20.0 ml. of water, and leaving in doubt whether the mineral had been decomposed by the excess of hydrofluoric acid used or by the subsequent fusion. Jannasch apparently realized the value of the molten fluoride but his interest was intrigued by his boric oxide flux—this fact and, possibly, a faulty translation, referring to his work, seem to have left this phase of the problem unnoticed ever since.

H. Rose[6] had previously proposed the following scheme, which had apparently been unfamiliar to Jannasch. To a mixture of ammonium fluoride and water in the form of a semi-fluid mass in a platinum crucible is added the finely ground sample of quartz or silicate. The mixture is then evaporated to dryness and ignited. It was stated (contrary to our experience with the dry reagent) that the process has to be repeated three to four times in the case of quartz but is more effective in the case of silicates. Rose's method is undesirable because of the time required in each treatment and the necessary repetition of the operation for complete reaction and because of loss from spattering due to the addition of water to the reaction mixture. Rose did not apply the method quantitatively.

Qualitative tests on finely powdered minerals—among them quartz, orthoclase feldspar, beryl, iron tourmaline—have shown that silica is rapidly eliminated in presence of molten ammonium fluorides. These results encouraged the writers to undertake a quantitative study on the extent of the decomposition. The quartz of glass sand was selected because of its simplicity of composition, its comparative resistance, among the silicon compounds, to attack by hydrofluoric acid, the availability of excellent analyzed samples, and the usefulness of a quick and accurate method of analysis for the commercial product. The samples analyzed were Bureau of Standards glass sand sample No. 81 and one that had been carefully analyzed, using the sodium carbonate fusion method, by one of the writers.?

Method of Analysis.—A weighed sample, previously dried at 110°, was thoroughly mixed with five grams of C. P. crystalline ammonium fluoride

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[4] J. J. Berzelius, *Lehrbuch der Chemie*, **3**, 282 (1856), Dresden.

[5] Jannasch, *Z. anorg. Chem.*, **12**, 220 (1896).

[6] Rose. *Pogg. Ann.*, **108**, 19 (1859).

[7] A. C. Shead, "Chemical Analyses of Oklahoma Mineral Raw Materials," Study No. 32, University of Oklahoma, Analysis No. 171.

in a tared *25.0* ml. platinum crucible, provided with a well-fitting lid which is kept in place during the subsequent decomposition. The crucible was placed in a hole through a heavy asbestos board of such a size that about a third of the surface of the crucible is exposed to the flame of an adjustable burner of the Tirrill type, and fixed at such a height that the bottom of the empty crucible will be maintained at a dull red heat. The fusion and expulsion of the excess reagent should require about ten minutes. Experience shows that about a gram of quartz of one hundred mesh or finer will be volatilized within this time but that a very small amount of silica will generally remain, necessitating the repetition of the process. The smallest residue of unattacked mineral is easily seen as it tends to segregate itself. The amount left will be large, even in the case of precipitated silica, unless the flux be thoroughly mixed with the sample, in the first place. The fusion is remarkably quiet and the small amount of residue spattering upon the lid can generally be easily removed by the following technique. The lid is heavily coated with ammonium salt upon which some of the residue may be projected. Toward the end of the fume evolution this coat is heated with the burner held in the hand and the flame impinging on the lid; this causes the detachment of the deposit, which falls into the crucible carrying the residue with it.

Before the crucible is allowed to come to redness, after the excess fluoride has been volatilized, it is advisable to add a drop or two of concentrated sulfuric acid, or a few fragments of ammonium bisulfate to prevent the escape of traces of iron or aluminum, as halide. Perchloric acid cannot be used, as ignition forms these halides.

TABLE I

TYPICAL RESULTS

Sample of glass sand	Sample, g.	Residue, g.	Residue, %	SiO_2 by difference, %
B. S. 81[a]	1.1741	0.0097	0.83	99.17
B. S. 81	1.0856	.0091	.84	99.16
B. S. 81	1.7514	.0057	.27	99.73
		Average	.65	99.35
B. S. 81	...	...	.74	99.26
Okla. 171	1.0088	.0017	.17	99.83
Okla. 171	1.2756	.0020	.16	99.84
Okla. 171	1.3905	.0021	.15	99.85
Okla. 171	0.7569	.0013	.17	99.83
		Average		99.84
Okla. 171	(By sodium carbonate fusion, etc.)			99.63

[a] Analysis of B. of S. sample No. 81: Fe_2O_3, 0.073; Al_2O_3, 0.265; TiO_2, 0.095; ZrO_2, 0.031; CaO, 0.029; MgO, 0.016; loss on ignition, 0.23. This gives a total of 0.74% impurities in the form finally weighed in these experiments. The indicated silica content is therefore 99.26%.

The time required for the expulsion of silica and excess reagents need not exceed twenty minutes, for both evaporations.

The residue is preponderantly oxides of iron, aluminum and titanium, with but negligible amounts of alkali and alkali earth oxides, and the loss can safely be attributed to silica in this particular case,

The data in Table I are typical of the results obtained.

Discussion

As ammonia fumes are given off copiously on heating ammonium fluoride, and a more fusible compound seems to be formed, it is suggested that the following reaction takes place

$$(NH_4)_2F_2 \textbf{ plus heat } \text{gives } NH_4F_2 \textbf{ plus } NH_3$$

Experiments with the technical grades of the bifluoride lead to the conclusion that previously fused pieces of this flux would probably afford prompter fusion, greater fluidity, a more acid nature and an even quieter melt than the normal salt.

Summary

Molten ammonium fluoride rapidly decomposes powdered quartz and silicates. This reaction has been proved to be quantitative, in the case of glass sand, and shows the possibility of opening silicates preliminary to determining other constituents therein, particularly the alkali metals.

URBANA, ILLINOIS
NORMAN, OKLAHOMA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

OXYGEN FILMS ON TUNGSTEN. I. A STUDY OF STABILITY BY MEANS OF ELECTRON EMISSION IN PRESENCE OF CESIUM VAPOR

BY I. LANGMUIR AND D. S. VILLARS

RECEIVED NOVEMBER 26, 1930 PUBLISHED FEBRUARY 9, 1931

In this paper we wish to describe a powerful method of studying the properties and detecting the presence of adsorbed films of oxygen on a tungsten surface. This method, not in general use, seems to us to be capable of much wider application than we are making of it here, and for that reason we wish to call it to the attention of chemists. We shall, at the same time, present evidence obtained by it to show that adsorbed oxygen films are held on a tungsten surface by enormous binding forces,[1] very much greater even than those corresponding to the heat of dissociation of the oxygen molecule.

The experimental work on which this paper is based was done by Dr.

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[1] Cf. Langmuir, Chandler Lecture, *Ind. Eng. Chem.*, 22, 393 (1930).

K. H. Kingdon; a part has already been published elsewhere.[2] In that article it was shown that minute traces of cesium vapor have a remarkable effect on the electron emission from a tungsten surface. Some of the most important data are summarized quantitatively in Fig. 1, which is Langmuir and Kingdon's Fig. 1. Consider, for example, the curve labeled 20°. This shows that the electron emission in the presence of cesium vapor saturated at 20° (0.001 barye) at low filament temperatures (the right side of the diagram, subsequently to be referred to as Region I) varies with increasing temperature according to the Richardson equation

$$i = AT^2\epsilon^{-b/T} \qquad (1)$$

up to about 640°K.,[3] but is many billionfold greater than that from pure tungsten. Thus at 590° ($10^3/T = 1.7$) the emission is $10^{-6.2}$ amp. cm.$^{-2}$, whereas that from pure tungsten would be the unmeasurable quantity 10^{-31}, if Dushman's[4] values of $A = 60.2$ and $b = 52,600$ are taken.

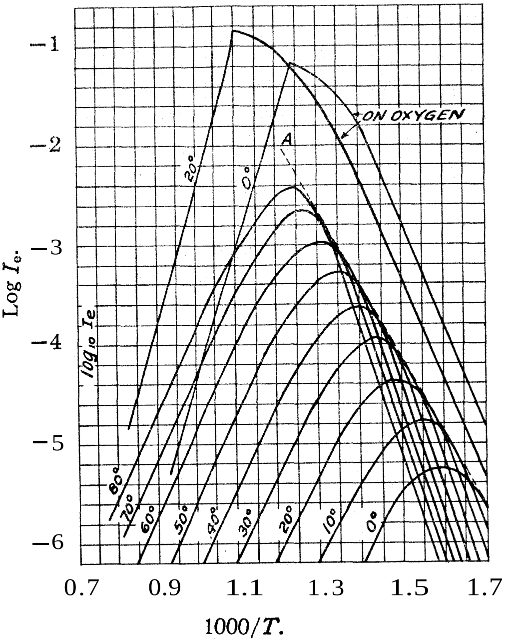

Fig. 1.—Electron emission from tungsten filaments in cesium vapor at various pressures (amps. cm.$^{-2}$)

On increasing the temperature from 640 ($10^3/T = 1.56$) to 715° ($10^3/T = 1.4$), the emission is found to pass through a maximum (Region II) and decrease with further increase in temperature (Region III). This drop in emission is due to an evaporation of the cesium from the surface. Finally, when all the cesium has evaporated off, the points on the curve bend upward again (with decreasing $1/T$) and the emission follows Equation 1.

The most remarkable phenomenon, however, was the effect of oxygen on these composite surfaces. Ordinarily, a layer of oxygen decreases the

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[2] I. Langmuir and K. H. Kingdon, "Thermionic Effects Caused by Vapors of Alkali Metals," *Proc. Roy. Soc.* (London), **A107,** 61–79 (1925).

[3] All temperatures, unless otherwise stated, will be given in absolute degrees, K. For the method of measuring temperature, the reader is referred to the article of Jones **and** Langmuir, Gen. Elec. *Rev., 30,* 310–319, 354–361, 408–412 (1927).

[4] S. Dushman, H. N. Rowe, J. Ewald and C. A. Kidner, *Phys. Rev.,* 25, 338 (1925).

emission from a pure tungsten surface. Thus, from Kingdon's data,[5] $A = 5 \times 10^{11}$ and b = 107,000, we calculate that the emission from an oxygen-coated surface should be 10^{-33} at 910° ($10^3/T = 1.1$) as compared with $10^{-17.4}$ from pure tungsten. If, now, cesium vapor is admitted to the oxygen-coated filament, the emission at all temperatures is increased so that at 910° it is $10^{-0.9}$, according to the curve in Fig. 1, marked "On Oxygen 20°." The general shape of the curve is the same as before, but now it obeys the Richardson equation up to much higher temperatures. The oxygen increases the stability of the cesium film, holding it much more firmly than tungsten does.

In all of these regions there is a balance between the rates of evaporation and of condensation of cesium on the surface, so that we may assume

$$\underset{\textbf{Rate of evaporation}}{k\Theta\epsilon^{-H_\Theta/RT}} = \underset{\textbf{Condensation}}{\alpha p\ (1 - €3)} \qquad (2)$$

Here 8 is the fraction of surface covered by the cesium atoms, H_Θ is the heat of evaporation, and p the vapor pressure of cesium. The transition Region II thus occurs close to the temperature at which the equilibrium value of 8 begins to be less than unity by a perceptible amount. Region I is that in which (1 – 8) is very small or 8 practically equal to unity. That this is true is also indicated by the fact that increasing the cesium vapor pressure affects the emission only slightly; in fact, decreases it instead of increasing it. Region III gives us the course of evaporation with the temperature.

Oxygen present on the surface produces two effects. One is a slight alteration of the work function, φ, through the cesium layer. The average work necessary to remove an electron from a surface is approximately a linear function of the fraction of the surface covered.

$$\varphi = \varphi_W + \Theta_{Cs}\,(\varphi_{W-Cs} - \varphi_W) \qquad (3)$$

where φ_W is the work function from a pure tungsten surface, φ_{W-Cs} is the corresponding work function from a tungsten surface covered with a complete layer of cesium, and Θ_{Cs} is the fraction of the surface covered with cesium. Evidence supporting this hypothesis has been discussed elsewhere.@ From Equations 1 and 3 it follows that log i is a linear function of Θ in view of the relation connecting b of equation 1 with φ

$$b = \varphi e/k = 11600\ \varphi \qquad (4)$$

if φ is given in volts. Although the work function from a Cs–O–W layer need not be exactly the same as that from Cs–W, this distinction is not very important, as may be seen from a study of Region I of the Cs–O–W and Cs–W curves (Fig. 1). The difference in log i, which, by Equation 1, depends principally upon the work function, is only 0.7 (at 590°), a small fac-

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[5] K. H. Kingdon, *Phys. Rev.*, 24, 510 (1924).

[6] I. Langmuir, *ibid.*, 22,357–98 (1922).

tor indeed when compared with the enormous differences we shall make use of later.

The other effect of the presence of an oxygen film is to hold cesium atoms which would otherwise evaporate under the same conditions of temperature and pressure. This effect comes to light in Region III where we no longer have the surface completely covered with cesium. Every oxygen molecule which strikes a bare tungsten surface is held so strongly that it cannot be dislodged at the low temperatures which are sufficient to evaporate cesium. These adsorbed atoms are, moreover, capable of holding cesium atoms much more tightly than the bare tungsten surface. A relatively high temperature is required therefore to bring about the evaporation of these cesium atoms to produce any given value of θ_{Cs}. It is this effect which allows us to go to much higher temperatures on the Cs–W curve of $\theta_{Cs} = 1$, without evaporating off all the cesium layer. This is the reason that oxygen can increase the emission 10^6 fold.

On first thought it is natural to assume that the curves labeled "On Oxygen" in Fig. 1 correspond to $\theta_O = 1$, where θ_O is the fraction of surface covered with oxygen. On the other hand, when we consider that, in the checkerboard arrangement of the surface, one oxygen adatom[7] may hold more than one cesium atom, perhaps as many as three to seven, our first hypothesis does not seem likely.

We may think of the total fraction of the surface covered by cesium, θ_{Cs}, to be made up of two parts, one of which is the fraction, θ'_{Cs}, which would naturally be present in equilibrium at that temperature if no oxygen were there, and the other of which is the additional fraction, θ''_{Cs}, held by the oxygen present.

$$\theta_{Cs} = \theta'_{Cs} + \theta''_{Cs} \tag{5}$$

It is then to be expected that the additional fraction held, θ''_{Cs}, should be directly proportional to the amount of oxygen present, up to a certain limit. For example, if the number of cesium atoms held by an oxygen atom were n, we would have

$$\theta''_{Cs} = n\theta_O \tag{6}$$

up to the point where $\theta_{Cs} = n\theta_O + \theta'_{Cs} = 1$. Beyond this value, the emission should be nearly constant, although θ_O might continue to increase to values all the way up to unity. For this reason we might expect the work function in Region III (where cesium is more or less evaporated off) to vary linearly with θ_O from 0 to about 0.33 (if $n = 3$), and be little affected by subsequent addition of oxygen to the surface. Notwithstanding this uncertainty in our knowledge of θ_O, we can probably be certain of one thing. Electron emissions of definite value below the maximum (at a

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[7] Becker, "The Life History of Adsorbed Atoms and Ions," *Trans. Am. Electrochem. Soc.*, *55*, *153–175* (1929), has suggested using the term "adatom" for an adsorbed atom.

fixed comparison temperature and cesium pressure) will correspond to a definite θ_O, no matter what evaporation procedure we have chosen to bring about this state.

Method of Procedure.—In this way, we have been able to develop a method of studying oxygen films on tungsten. First, a well-aged tungsten filament is flashed in vacuum for two seconds, at a temperature of 2700°, to clean its surface completely. It is then allowed to cool to room temperature, and cesium vapor at a pressure of 0.0024 barye (saturation pressure at 28°) is admitted.[8] This instantly (within about one second)[9] forms a complete layer on the tungsten surface and increases the electron emission from values too small to measure to those easily measured in the temperature range 550–900° (see Fig. 1). To produce the film of oxygen which we propose to study, we raise the temperature of the filament to around 2000°, thus evaporating off all the cesium, surround the bulb with liquid air to lower the cesium vapor pressure to an infinitesimal amount, and admit oxygen, at 0.1 mm. pressure, covering the surface with a complete layer of the latter. The filament is then allowed to cool to room temperature, any residual oxygen is pumped out and cesium vapor is again admitted by simply removing the liquid air from the bulb. On now heating the fila-

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[8] This may be readily done in one of two ways. If a high frequency induction outfit is available, a nickel capsule containing a mixture of cesium dichromate and silicon may be placed in a side arm of the tube (pyrex). The whole may be baked out at as high a temperature as desirable, after which the cesium is liberated by bringing the nickel to a red glow by means of the high frequency coil. If the latter is not available, a second method is to use a mixture of metallic calcium and cesium chloride. The tube (lime or hard glass) may not be baked out at temperatures above 350° as the calcium would begin to react. When ready to drive over the cesium, the temperature is increased by heating with a Bunsen flame. This method has disadvantages over the first one in that the baking temperature may not be as high, and that the reagents, being hygroscopic, are apt to become contaminated while being handled.

[9] We calculate that a fraction of cesium on the surface of $\theta_{Cs} = 10^{-5}$ may be readily detected by using a galvanometer ballistically and determining the positive ion emission while flashing the filament to 1500°. (All atoms on the filament pass off instantaneously as positive ions during the flashing if submitted to sufficient accelerating potential, say, 45 v.). An ordinary galvanometer has a sensitivity such that 10^{-9} coulombs will give a kick of 1 cm. This is equivalent to 6.3×10^9 positive ions. A surface completely covered with cesium contains 4 X 10^{14} atoms cm.^{-2}. Thus, the fraction readily detected is $\theta_{Cs} = 6.3$ X $10^9/4$ X $10^{14} = 1.57$ X 10^{-5}. If n cesium atoms were held by each oxygen atom present, one could readily detect $\theta_O = 1.57$ X $10^{-5}/n$. This suggests that an extremely powerful method of studying surfaces of low 8 is to choose a cesium pressure low enough for the constant positive ion current to be small, and a filament temperature such that $\theta'_{Cs} = 0$. By making the filament positive with a sufficient voltage, all cesium atoms striking the surface will be instantaneously changed to cesium ions and flow to the cathode. This current should be balanced out of the galvanometer. If there were a small trace of oxygen on the filament, θ''_{Cs} would have a definite value, which could be determined by flashing the filament. The ballistic kick then will tell one how great is θ''_{Cs} and the relative value (although not absolute) of θ_O.

ment to temperatures from 600 to 1200°, with positive voltage on the anode, no measurable electron emission is detected. To get the typical electron emission from the adsorbed cesium film, it is first necessary to "activate" the oxygen film. The maximum activation is produced by flashing the filament for a few seconds at temperatures from 1600 to 1800°, the exact temperature and time being of little importance.

After activation, the filament, in the presence of cesium vapor at 20°, gives at 650° an emission which is roughly only five times as great as before the oxygen film was produced. The activated oxygen film, however, allows us to raise the filament temperature to 850° or even 900° before losing enough of the adsorbed cesium to cause a decrease in emission. Under these conditions, the currents are 10^5 or 10^6 times greater than in the absence of the oxygen film.

We propose to use this increase as a measure of the amount of adsorbed oxygen and in this way study the rate of evaporation of these oxygen films.

In the absence of cesium vapor, the effect of oxygen is to decrease greatly the electron emission from tungsten. This change in emission can also be used to detect and study oxygen films, and has been used in the work to be described in the second paper of this series. The method has, however, the disadvantage that even at 1700° the emission from an ordinary filament is less than 10^{-8} ampere and at temperatures as high as this the films may evaporate somewhat even during the measurements. With cesium vapor, not only can much smaller amounts of oxygen be detected, but the tests for the oxygen are made at such low temperatures that no evaporation occurs.

This qualitative test becomes quantitative as soon as we know the law by which θ''_{Cs} depends on θ_{O} (Eq. 6). Until then we may reproduce at will particular values of θ_{O} without having more than approximate knowledge of their absolute magnitude.

In our studies of the evaporation of the films, the oxygen-covered filament was heated at a definite "evaporation temperature" for successive time intervals. After each heating to the evaporation temperature, the filament was cooled and the condition of its surface was then determined by measuring its electron emission[10] at a series of "test temperatures" ranging from 802 to 1092°

Similar data were obtained at other temperatures. By comparing the rapidity of the deactivation at various evaporation temperatures, as revealed by the changes in emission at any given test temperature, we can obtain the relative temperature coefficients of the rates of evaporation.

It was shown by Langmuir[11] that the rate of evaporation m is related to

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[10] This method is similar to that used by Langmuir in his study of thoriated tungsten filaments, *Phys. Rev.*, 22, 357–398 (1923).

[11] I. Langmuir, *ibid.*, 2, 329 (1913).

the vapor pressure, p, of a substance by the equation

$$m = (1 - r)\,(M/2\pi RT)^{1/2}p \tag{7}$$

where M is the atomic or molecular weight and r is the reflection coefficient of incident atoms. In the present case, from evidence that will be discussed in later papers of this series, we believe that r is small and has no appreciable temperature coefficient. Thus the temperature coefficient of the rate of evaporation is approximately the same as that of the vapor pressure (neglecting the factor $T^{1/2}$). In this way by the Clapeyron equation we may determine the heat of evaporation of adsorbed oxygen from the temperature coefficient of the rate of evaporation.

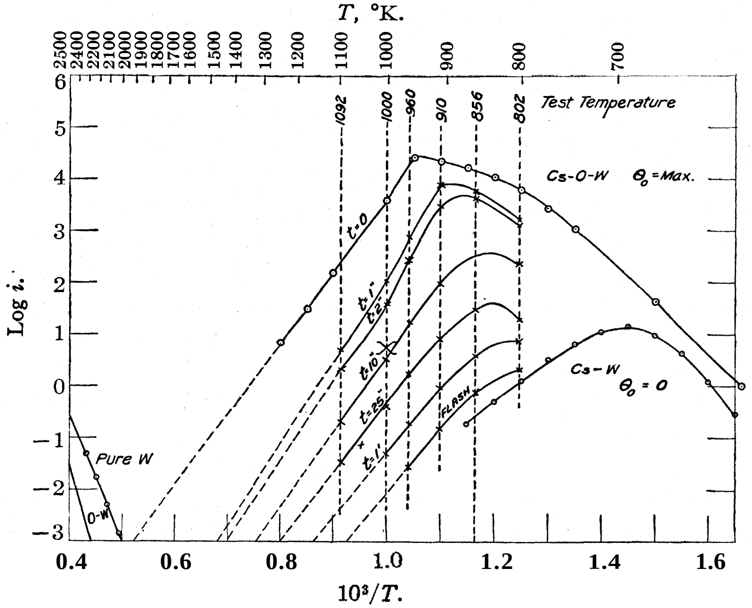

Fig. 2.—Electron emission from Cs–O–W surfaces of varying oxygen and cesium content. Total emission from 50-mm. 4-mil wire (0.01016 cm. diam.) in microamperes. O, Values from other data2 calculated to wire of area used (0.1598 sq. cm.). X, Experimental values. Cesium vapor pressure, 0.00246 baryes (28 °C.). *t* is time of oxygen evaporation at 2070 °K.

Experimental Data.—The experimental data on the electron emission from Cs–O–W surfaces of varying θ_O for one characteristic evaporation temperature are given in Fig. 2. Each of these curves corresponds to a definite time of evaporation of oxygen at 2070°. A similar set of curves was obtained for two lower evaporation temperatures, 1978 and 1856". As these curves have the same appearance as those in Fig. 2, we shall not reproduce them here. To get the temperature coefficient of the rate of evaporation, and from it the heat of evaporation, one might pick the point X in Region III, half-way between the top and bottom curve, and compare the evaporation time which gives a surface of that electron emission at that particular test temperature, with the evaporation time at the next evaporation temperature (1978°) which gives the same electron emission at the same test temperature. From what has been said above, it is reasonable that the surface is the same in both cases. As may be seen from Fig. 2, this arbitrary half-way curve was not among those determined experimentally. The time which would give this curve may be determined by any method of interpolation. That method which gives a straight line is, however, always the most convenient. From the logarithmic[12] form of Equation 2.

$$-\frac{\mathrm{d}\ln\Theta}{\mathrm{d}t} = k\epsilon^{-H_\Theta/RT} = k' \qquad (8)$$

we see that if H_Θ is constant, a plot of log A, where $A \equiv \log i - \log i_0$ and i_0 is the emission from the cesiated surface of $\Theta_0 = 0$, against evaporation time, t, should give us this straight line, in view of the relation between A and Θ (Equations 1, 3 and 4).

$$\frac{\mathrm{d}\ln\Delta}{\mathrm{d}t} = \frac{\mathrm{d}\ln\Theta}{\mathrm{d}t} \qquad (9)$$

The "half life"[13] may then be determined from the curve by inspection. Plotting log $t_{1/2}$ against $1/T$ would now give us a curve the slope of which is a measure of the heat of evaporation. Figure 3, in which is plotted log Δ against t for four different test temperatures, shows that these curves are essentially straight, at least in the Θ region studied in these experiments. The velocity constant k' is then related to the time of half evaporation by the equation

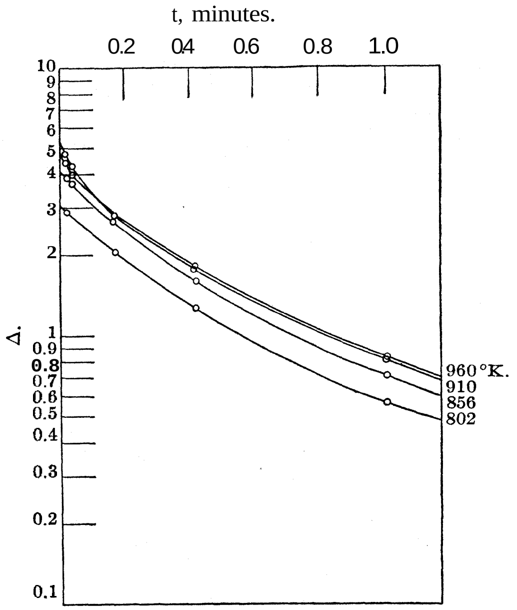

Fig. 3.—Course of evaporation with time at 2070°K., as measured at test-temperatures indicated. $\Delta \equiv \log i - i_0$ and is proportional to the covering fraction, Θ_0.

$$t_{1/2} = (\ln 2)/k' \qquad (10)$$

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[12] In this and following papers we **shall** follow the customary notation in which log designates the common logarithm and ln the natural logarithm.

[13] This "half life," in view of the consideration involved in Equation 6, does not necessarily mean the time it takes for Θ_0 to reach 0.5. It is the evaporation time it takes to obtain surface conditions such that, at the particular test temperature used. the sum $\Theta'_{Cs} + \Theta''_{Cs} = 0.5$.

A closer inspection of Fig. 3, however, reveals the fact that the half times obtained at different test temperatures are slightly different. In this example they are 0.27, 0.23, 0.32 and 0.33 minutes at the test temperatures 960, 910, 856 and 802°, respectively. It is obvious that some method of averaging must be resorted to if we are to get the best value of the temperature coefficient of evaporation. In doing this we have not limited ourselves to determining the half time, but have compared the times it takes for the surface to reach other stages of evaporation as well. Table I gives these evaporation times in minutes for different evaporation temperatures, test temperatures and A (proportional to Θ). We might next proceed to plot log t against $1/T$ for each separate set of times to reach the same stage of evaporation and find the average slope of all of these straight lines, but it is much simpler to reduce all times to values relative to that at the evaporation temperature 1978° as unity, average them, and plot the single set of three points. We have chosen the latter procedure.

TABLE I

EVAPORATION TIMES

Test temp , 802°K. ($A_,$ = 0.15)

	Evaporation temp., °K.				
Δ	1856 Minutes	1078 Minutes	2070 Minutes	t_{1856}/t_{1978}	t_{2070}/t_{1978}
0.8	81.8	6.90	0.714	11.85	0.1034
9	66.9	5.42	.632	12.34	.1166
1.0	55.9	4.29	.561	13.03	1308
1.2	38.5	3.12	.454	12.34	.1455
1.5	29.1	2.07	.327	14.06	.1590
2.0	13.2	1.15	.181	11.48	.1574
Test temp., 856° (A_a = 0.175)					
0.9		7.52	0.811		0.1078
1.1	78.0	4.76	664	16.39	.1395
1.5	40.7	2.81	457	14.48	.1626
2.0	24.7	1.74	.304	14.19	.1652
2.5	13.1	1.17	.192	11.20	.1641
Test temp., 910° ($A_,$ = 0.20)					
1.3	76.4	4.61	0.636	16.57	0.1379
1.5	53.8	3.52	533	15.28	.1514
2.0	32.2	2.07	352	15.56	.1701
2.4	19.9	1.47	.245	13.54	.1667
Test temp., 960° ($A_,$ = 0.225)					
1.3	72.2	5.08	0.653	14.22	0.1286
1.5	50.7	3.53	.447	14.36	.1266
1.9	33.7	2.28	.384	14.78	.1684
2.3	19.9	1.63	.273	12.21	.1675
				Mean 13.77	0.1458

A = log i_O − log i, where i = electron emission from Cs–O–W surface of $\Theta_O = x$, and i_O = emission from Cs–W surface of $\Theta_O = 0$. $A_,$ = amperes at which filament a was run during emission readings. t_{1856}/t_{1978} = evaporation time relative to that at temperature 1978°.

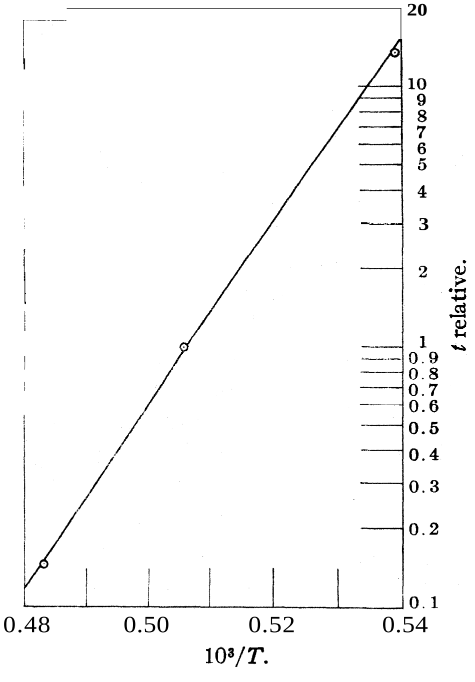
TABLE II

TEMPERATURE COEFFICIENT OF EVAPORATION

T, °K.	$t_{1/2}$, min.	t_{relative}	$10^4/T$
1856	27	13.77	5.39
1978	2	1.00	5.06
2070	0.3	0.146,	4.83

Thus Columns 5 and 6 of Table I give the relative times for each determination. These are averaged and given in Table II.

The heat of evaporation corresponding to the slope of the log $t_{\text{av.}}$ *versus* $1/T$ plot (Fig. 4) is 162 kg. cal. This is the heat per gram molecule of the substance dissociated. If the oxygen comes off in the form of atoms, as we have reason to believe, it is the heat per gram atom of oxygen. This is some 2.5 times the heat of dissociation of oxygen[14] (per gram atom). It is no wonder, therefore, that a bare tungsten surface has such a power of taking up oxygen. The practically constant slope of the curves in Fig. 3 indicates that we are taking our measurements in a region where H_Θ is independent of Θ. We conclude therefore that 162 kg. cal. is most probably the heat of evaporation from a surface almost bare ($\Theta_O \sim 0.15$). In a later paper we shall present data from a Θ region between 0.35 and 0.7 which show that H is less than 162 kg. cal., and decreases with increasing Θ.



Slope equivalent to H = 162 kg. cal.

Fig. 4.—Relative evaporation time.

Concluding Remarks.—In the foregoing pages we have presented a method of studying the rate of loss of adsorbed oxygen from tungsten. Since this consists primarily in detecting the amount of oxygen on the surface, it may be used equally well for studying

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[14] Taking the heat of dissociation of oxygen per gram molecule to be 131 kg. cal., Rodebush and Troxel, THIS JOURNAL, 52, 3467 (1930); Copeland, *Phys.* Rev., **36,** 1221–1231 (1930).

the accumulation of oxygen. As an illustration in this connection, we refer to the difficulty of Rodebush[15] and his co-workers in finding a suitable method of detecting beams of oxygen molecules or atoms. We suggest that these could be readily identified by an adaptation of the above procedure. A beam of molecules impinging on a hot (1600°) clean (by preliminary flashing to 2700°) tungsten filament will deposit with almost one hundred per cent. efficiency until the surface has received its maximum sensitivity. The deposition of oxygen molecules on a cold surface does not affect the emission in the presence of cesium vapor. It is almost certain (it has not been tried) that a beam of oxygen atoms impinging on a cold surface will modify its subsequent emission in cesium vapor to the same extent as a molecular beam hitting a hot surface. If this is true, we have a method of distinguishing between atomic and molecular oxygen.

If a layer of $\Theta_O = 0.33$ ($n = 3$ in Equation 6) gives the maximum emission ($10^6 \times$ the Cs–W emission), then a layer of $\Theta_O = 0.33 \times (\log 2)/(\log 10^6) = 0.017$ will cause a doubling of the emission, which certainly can be readily detected. A beam of the density ordinarily used in molecular ray experiments will deposit a complete layer in about one second.[16] It therefore would take only 0.017 second to deposit out of such a ray enough oxygen to be readily detected. These rays usually originate from enclosures in which the pressure is 0.1 mm. It may be seen that with such a sensitivity much lower pressures may be used, with the consequence that the beam can be better resolved. Hitherto, the most hopeful method of detecting oxygen beams seems to have been that of Knauer and Stern,[17] who have a small box with an entrance consisting of a slit which may be moved back and forth across the beam. By measuring the pressure change in the box, the distribution of intensity in the beam may be determined. Up to now this is the only practical method invented to detect beams of inert gases, but this need no longer apply to the case of oxygen. The use of a movable tungsten wire in detecting beams is not only a much more simple method, but is also practical, as has been demonstrated by Taylor,[18] who detected cesium beams by the positive ion current from a wire mounted on a contrivance capable of moving it across the beam.

We wish to acknowledge our indebtedness to Dr. K. H. Kingdon for the experimental data which we have used and to Mr. Saunders MacLane, who gave valuable assistance in analyzing these data.

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[15] Rodebush and Nichols, THIS JOURNAL, 52,38643868 (1930).

[16] Pressures as low as 10^{-7} baryes would bring about the deposition of a layer of $\Theta = 1$ in about five hours. On account of this extreme sensitivity, all stray oxygen would have to be removed from the apparatus. This would be readily done, we believe, by the cesium vapor present under the conditions of the experiment.

[17] F. Knauer and O. Stern, *Z. Physik,* 53, 766 (1929).

[18] J. B. Taylor, *ibid.,* 57, 242–248 (1929).

Summary

A method is presented of studying the rate of loss of oxygen from an adsorbed film on tungsten, as well as of detecting its presence in a gas. This consists in observing its effect on the electron emission of a tungsten filament, sensitized by the presence of minute traces of cesium vapor (10^{-6} mm.). Under properly chosen conditions a monatomic oxygen film makes its presence known by increasing the emission a millionfold.

Using this method, the heat of evaporation of oxygen from the adsorbed layer was found to be 162 kg. cal. (7.0 v.) per gram atom.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 69]

THE ADSORPTION OF GAS MIXTURES BY SILICA

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RECEIVED NOVEMBER 28, 1930 PUBLISHED FEBRUARY 9, 1931

Introduction

Studies of the adsorption of gases by catalytically active solids, particularly in the last decade, have contributed greatly to a qualitative understanding of the kinetics and mechanism of contact catalysis. Frequently, however, more than one of the reactants or products are simultaneously adsorbed, and in such cases it is obviously necessary to have information concerning the adsorption of one gas in the presence of a second. Such data should also be useful in connection with the practical problem of separating the components of a mixture of gases or vapors. In addition, the behavior of mixtures may be expected to furnish a deeper insight into the nature of adsorption.

Comparatively little is known about the adsorption of the individual constituents of gas mixtures. Richardson and Woodhouse[1] studied the adsorption of carbon dioxide–nitrous oxide mixtures on charcoal. With their static method, however, the composition of the gas phase and of the adsorbed layer can be estimated only approximately. Klosky and Woo,[2] employing the flow method, have studied the adsorption of sulfur dioxide–butane and sulfur dioxide–methyl chloride mixtures on titania gel. Their results indicate that the presence of a second gas decreases the amount of the first gas adsorbed. Other recent studies on the adsorption of gaseous mixtures are those of Putnoky and Szelényi[3] on ethanol–ether–air mixtures with various silica gels, and of Frolich and White[4] on mixtures of methane and hydrogen at elevated pressures in contact with charcoal.

[1] Richardson and Woodhouse, THIS JOURNAL, 45, 2638 (1923).

[2] Klosky and Woo, *J. Phys. Chem.*, 32, 1387 (1928).

[3] Putnoky and Szelényi, *Z. Elektrochem.*, 34, 805 (1928); 36, 10 (1930).

[4] Frolich and White, *Ind. Eng. Chem.*, 22, 1058 (1930).

From the standpoint of contact catalysis it would be more interesting to study the adsorption of mixtures by catalytically active adsorbents than by such materials as charcoal and titania gel. Griffin[5] has shown that the presence of a small amount of carbon monoxide, less than 0.05 cc., upon a sample of catalytically active copper, increases the amount of hydrogen adsorbed at low pressures but decreases the amount adsorbed at higher pressures. This is an indication of the complexity of adsorption of gas mixtures by active catalysts.

As a preliminary investigation to the study of mixture adsorption by active catalysts it seemed advisable to investigate first the behavior of a solid which normally shows adsorptions of the "secondary," or non-selective, type. Silica was chosen as a suitable material, since previous work[6] has shown that its behavior with a number of gases is of the type in question.

Carbon monoxide, carbon dioxide and oxygen were selected because silica does not induce interaction between any of these at the temperatures used, yet it adsorbs convenient amounts of each, a small amount of oxygen, a large amount of carbon dioxide and an intermediate amount of carbon monoxide.

Experimental Procedure

The apparatus used in this investigation is illustrated in Fig. 1. The entire apparatus up to G and H, including the gas generators and purifying lines, was constructed of pyrex glass, all joints being fused. The pyrex-to-soft glass seals (G, H) were effected by surrounding the ends of the tubing by glass cups which were filled with deKhotinsky cement. The adsorbent was contained in bulb B, which could be maintained at either 0 or 100° by an ice- or steam-bath. The pressure in bulb B was determined by the mercury manometer M. A Topler pump, T, was connected as indicated to bulb B and to the calibrated gas buret A, the latter being connected to the buret of a modified Orsat gas analysis apparatus (not shown).

The individual gases from the generators and purifying lines (not shown in Fig. 1), entering at C, D, E, could be passed directly over the adsorbent in B, or into any of the three mixture reservoirs, only one of which is shown in the figure (1, 2). From these reservoirs the mixtures passed over calcium chloride and phosphorus pentoxide, respectively, in X and Y, and thence through bulb B, or to buret A for analysis. Freshly boiled water was used as the confining liquid in the reservoirs, except for mixtures containing carbon dioxide, for which a concentrated solution of magnesium sulfate was preferable on account of the diminished solubility of carbon dioxide.

The mixtures were passed over the adsorbent in bulb B for about two hours, the pressure in the bulb being maintained at exactly 760 mm. by regulation of the head of concentrated sulfuric acid in N. The failure of the manometer M to denote any change of pressure within the bulb after standing for an hour or more after it was closed off by stopcocks indicated that equilibrium had been reached. As a further check on the establishment of equilibrium, mixtures were passed over the adsorbent in one case for fifteen minutes and in a second case for two hours, the same adsorption being obtained

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[5] Griffin, THIS JOURNAL, 49, 2136 (1927).

[6] Benton, *ibid.*, 45, 887 (1923).

in each instance. After equilibrium was reached the gas was removed from the bulb by means of the Topler pump and forced into the gas buret A, where its volume was determined. From this buret it was passed into the gas analysis apparatus.

The isotherms of the individual gases were determined by streaming the pure gas over the adsorbent until equilibrium was reached. Successive small amounts of gas were pumped out of the bulb by means of the Topler pump and the volumes read in the buret. After each removal of gas the pressure in the bulb was determined by means of the mercury manometer after it had become constant, thus indicating that equilibrium had been reached.

All adsorptions were repeated and the results duplicated to within an average of about 0.05 cc., with the exception of mixtures containing carbon dioxide. In such mixtures the solution of carbon dioxide in the confining liquid in the reservoir caused a progressive change which made it impossible to carry out duplicate runs with mixtures of identical composition. All gas analyses were run in duplicate and checked to within one-tenth of one per cent., and in most cases to within a few hundredths of one per cent.

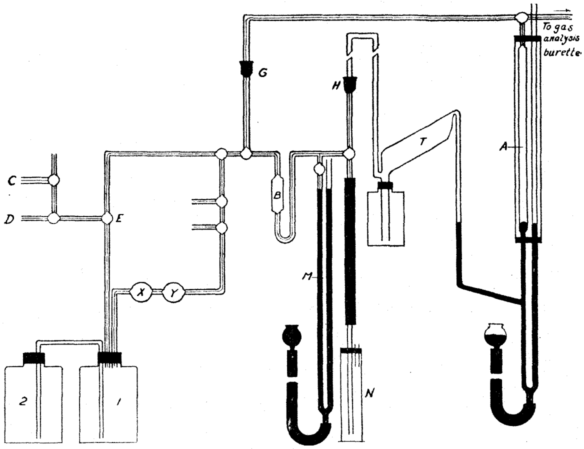

Fig. 1.—Apparatus.

The free space in the bulb was determined by measuring the amount of helium necessary to fill it at a pressure of 760 mm. and at temperatures of 0 and 100°. It is assumed that helium was not adsorbed by the silica.

The adsorptions of the separate gases are calculated by taking the difference between the volumes of the gas in question and of helium required to fill the bulb containing the adsorbent at a given temperature and pressure. In the case of mixtures the amount of each component adsorbed is obtained as follows. From the total volume of gas pumped out of the bulb, and its analysis, the total volume of each component present (that is, gas adsorbed plus gas in free space) is known. The amount of each component in the free space is obtained from the analysis of the mixture which is passed over the adsorbent, together with the volume of the free space as determined with helium. By subtraction of the amount of each gas in the free space from the total amount of that gas present, the quantity adsorbed may be calculated. All pressures have been expressed in mm. of mercury at 0°, and volumes in cc. at 0°, 760 mm.

Oxygen was prepared by electrolysis of a solution of sodium hydroxide between nickel electrodes. Carbon monoxide was generated by dropping concentrated sulfuric acid on hot 85% formic acid solution. Carbon dioxide was obtained by dropping sulfuric acid into a concentrated solution of chemically pure sodium bicarbonate. To each generator were attached the usual devices for removing spray and for purifying and drying the gases.

The adsorbent was prepared by prolonged washing of C. P. precipitated silicic acid and subsequent heating to 250° for a period of several days. The sample of adsorbent weighed 19.6 g.

Experimental Results

Isotherms for Individual Gases.—The isotherms of oxygen and of carbon monoxide have been determined at 0 and at 100°. Since inconveniently large amounts of carbon dioxide are adsorbed at 0° the isotherm for this gas has been determined only at 100°. The experimental data are recorded in Tables I and II. Pressures are expressed in mm. of mercury at 0°, and volumes are in cc. at 0° and 760 mm. The calculated values recorded in these tables will be discussed in a later section.

All the measurements with carbon monoxide and oxygen, both singly and in mixtures of the two, were completed before any carbon dioxide was used. All the values so obtained were found to be accurately reproducible, regardless of the order of the experiments. On first employing carbon dioxide, however, the adsorptive capacity of the silica for this gas underwent a gradual increase of about 6 cc. during nine successive runs, after which it remained constant for three additional runs. It was then found that the adsorptive capacity for oxygen had been slightly increased, while it had remained unchanged for carbon monoxide. From this point on, the new values were accurately reproducible. Because of the above effects it is necessary in comparing adsorptions in mixtures with those of the separate gases, to use the data headed "100° (before CO_2)" in Table I for comparison with oxygen–carbon monoxide mixtures, and those headed "100° (after CO_2)" for comparison with oxygen–carbon dioxide mixtures.

It is not known whether or not the increase in adsorptive capacity produced by repeated treatments with carbon dioxide is due to a displacement of water from the silica.

TABLE I

ADSORPTION OF OXYGEN BY SILICA (19.6 G.)

	0°		100° (before CO_2)			100° (after CO_2)		
	Volume adsorbed			(Volume adsorbed			Volume adsorbed	
Press., mm.	Obs., cc.	Calcd., cc.	Press., mm.	Obs., cc.	Calcd., cc.	Press., mm.	Obs., cc.	Calcd., cc.
83.0	3.32	3.27	17.9	0.08	0.12	40.4	0.37	0.29
142.4	5.57	5.57	88.6	.54	.60	139.1	1.00	.99
224.3	8.73	8.71	133.9	.90	.91	204.1	1.40	1.45
329.6	12 68	12.67	221.9	1.52	1.51	260.9	1.77	1.85
405.1	15 48	15.48	329.0	2.19	2.22	361.7	2.53	2.55
544.1	20.42	20.49	417.1	2.87	2.81	428.7	3.04	3.01
602.5	22.48	22.56	471.4	3.18	3.17	527.3	3.69	3.69
667.5	24.86	24.84	570.5	3.92	3.82	608.4	4.25	4.24
760.0	28.03	28.04	653.2	4.38	4.36	760.0	5.26	5.26
			760.0	5.01	5.05			

TABLE II

ADSORPTIONS OF CARBON MONOXIDE AND DIOXIDE BY SILICA (19.6 G.)

CO at 0°			CO at 100°			CO_2 at 100°		
	Volume adsorbed			Volume adsorbed			Volume adsorbed	
Press., mm.	Obs., cc.	Calcd., cc.	Press., mm.	Obs., cc.	Calcd., cc.	Press., mm.	Obs., cc.	Calcd., cc.
95.5	7.09	7.08	26.3	0.26	0.29	26.3	3.37	3.46
127.4	9.48	9.38	127.9	1.37	1.38	77.6	10.07	10.05
199.7	14.37	14.46	224.4	2.36	2.38	114.9	14.73	14.71
272.4	19.41	19.41	321.0	3.37	3.34	141.1	17.94	17.92
367.4	25.54	25.64	434.5	4.42	4.44	190.8	23.93	23.88
463.7	31.70	31.70	537.2	5.30	5.39	239.9	29.61	29.60
549.7	37.01	36.91	639.4	6.33	6.31	289.0	35.18	35.16
647.9	42.65	42.63	760.0	7.40	7.35	332.8	40.02	39.99
760.0	48.89	48.88				378.4	44.82	44.89
						434.8	50.76	50.79
						477.3	55.05	55.11
						536.8	61.01	61.00
						593.1	66.40	66.40
						689.1	75.47	75.25
						760.0	81.78	81.51

Adsorption of Mixtures.—The adsorption of each gas in mixtures of carbon monoxide and oxygen has been determined at 0 and at 100°. The adsorption of each gas in mixtures of carbon dioxide and carbon monoxide and in mixtures of carbon dioxide and oxygen has been determined only at 100°.

The results obtained are recorded in Tables III to VI. The pressures of each gas in the various mixtures are given in the first and second columns. The values recorded in the third and sixth columns are the volumes which would be adsorbed at the pressures given if the second gas were not present, as determined by interpolation from the isotherms for the individual gases.

TABLE III

$CO-O_2$ MIXTURES AT 0°

		Volume of oxygen adsorbed			Volume of carbon monoxide adsorbed		
p_O	p_{CO}	Isotherm	Obs.	Calcd.	Isotherm	Obs.	Calcd.
230.2	529.8	8.98	8.31	7.96	35.90	35.02	35.00
391.1	368.9	15.05	14.10	13.79	25.82	24.69	24.84
585.1	174.9	21.93	21.73	21.12	12.80	11.63	12.06

TABLE IV

$CO-O_2$ MIXTURES AT 100°

		Volume of oxygen adsorbed			Volume of carbon monoxide adsorbed		
p_O	p_{CO}	Isotherm	Obs.	Calcd.	Isotherm	Obs.	Calcd.
210.3	549.7	1.45	1.56	1.30	5.50	5.27	5.46
286.4	473.6	1.95	1.96	1.79	4.80	4.40	4.75
335.7	424.3	2.30	2.33	2.11	4.34	4.05	4.29
548.9	211.1	3.73	3.72	3.55	2.24	2.16	2.19

TABLE V

CO_2–O_2 MIXTURES AT 100°

p_O	p_{CO_2}	Volume of oxygen adsorbed Isotherm	Obs.	Calcd.	Volume of carbon dioxide adsorbed Isotherm	Obs.	Calcd.
182.5	577.5	1.30	1.81	1.10	64.90	65.14	64.45
199.0	561.0	1.42	1.78	1.21	63.40	63.89	62.84
438.6	321.4	3.08	2.90	2.81	38.70	38.82	38.04
614.1	145.9	4.30	4.25	4.10	18.70	18.65	18.02
618.0	142.0	4.32	4.21	4.13	18.20	18.45	17.55

TABLE VI

CO_2–CO MIXTURES AT 100°

p_{CO}	p_{CO_2}	Volume of carbon monoxide adsorbed Isotherm	Obs.	Calcd.	Volume of carbon dioxide adsorbed Isotherm	Obs.	Calcd.
211.6	548.4	2.34	2.98	1.93	62.10	61.51	60.13
259.5	500.5	2.73	3.21	2.38	57.50	57.30	55.16
377.0	383.0	3.89	3.77	3.50	45.40	45.42	42.75
384.9	375.1	3.97	3.70	3.57	44.50	44.68	41.90
555.0	205.0	5.55	5.53	5.25	25.60	25.93	23.32

The volumes actually adsorbed in the mixtures are given in the fourth and seventh columns headed "observed." The fifth and eighth columns headed "calculated" will be discussed in a later section.

Discussion

Adsorption of Single Gases.—Langmuir,[7] assuming adsorption in a unimolecular layer on a plane surface, has derived an equation of the general form

$$V = V^\circ \frac{ap}{1 + ap} \tag{1}$$

where V is the volume of gas adsorbed at pressure p, a is a constant at a given temperature, and V° is the saturation value, or the amount of gas adsorbed when the surface is entirely covered. This equation may be written in the form

$$1/V = (1/aV^\circ)(1/p) + (1/V^\circ)$$

If this equation holds, a plot of $1/V$ against $1/p$ should yield a straight line whose slope and intercept should permit a calculation of a and V°.

In Figs. 2 and 3 are shown the plots of $1/V$ against $1/p$ for the various gases at the two temperatures. It is evident that Equation 1 is satisfactory. The values of V° and a thus obtained are given in Table VII.

The values calculated from Equation 1, with the constants of Table VII, are given in Tables I and II under the columns headed "calculated."

Although Equation 1 agrees with the experimental data within the estimated limits of error at almost every point, it must nevertheless be

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[7] Langmuir, THIS JOURNAL, 40, 1361 (1918).

TABLE VII

CONSTANTS IN ADSORPTION EQUATION

Gas and temperature	$V°$, cc.	a, mm.$^{-1}$
O_2 at 0°	397.0	0.000100
CO at 0°	322.6	.000235
O_2 at 100°, before CO_2	171.3	.000040
O_2 at 100°, after CO_2	153.9	.0000466
CO at 100°	60.2	.000183
CO_2 at 100°	426.4	.000311

regarded as purely empirical, since V_0, the saturation value, is widely different not only for different gases but for the same gas at different temperatures. Owing to the fact that in these experiments ap is small compared to unity, that is, that the volume adsorbed is so nearly proportional to the pressure, only the product aV^0 can be estimated accurately,

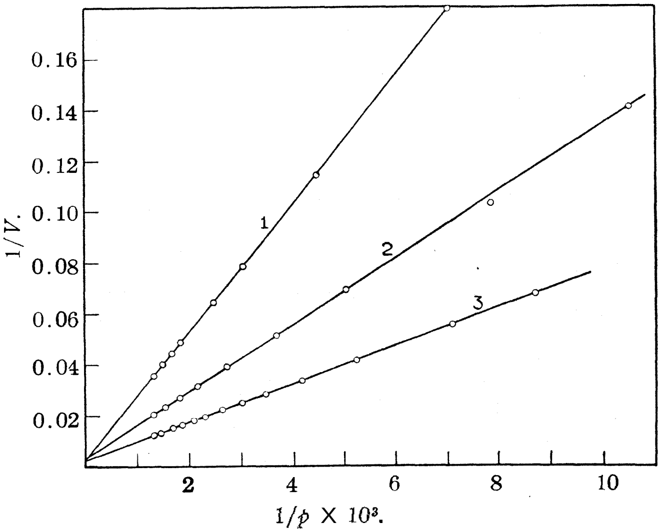

Fig. 2.—Variation of $1/V$ with $1/p$ for the adsorption of oxygen at 0° (Curve 1), carbon monoxide at 0° (Curve 2), carbon dioxide at 100° (Curve 3).

while a and $V°$ are each subject to considerable uncertainty. The errors in the values of V^0 thus introduced are enormously less than the differences shown in Table VII. It is obvious, however, that the equation could be more adequately tested by extending the measurements to higher pressures.

Adsorption in Binary Mixtures.—If it is assumed that the surface of the adsorbent is uniform and capable of adsorbing only a single layer of gas, and, furthermore, that there is no interaction between the adsorbed gases, an equation can be derived which relates the amount of one gas adsorbed to its pressure and to the pressure of the second gas.

Let σ_1 and σ_2 represent the fractions of the surface covered by Gases 1 **and 2,** respectively. The rate of condensation of Gas 1, μ_1, is equal to $k_1p_1\ (1-\sigma_1-\sigma_2)$, where $(1-\sigma_1-\sigma_2)$ is the fraction of the surface free from gas, p_1 is the pressure of Gas 1, and k_1 is a constant at a given temperature. The rate of evaporation, ν_1, can be expressed by the equation $\nu_1 = k_1'\sigma_1$.

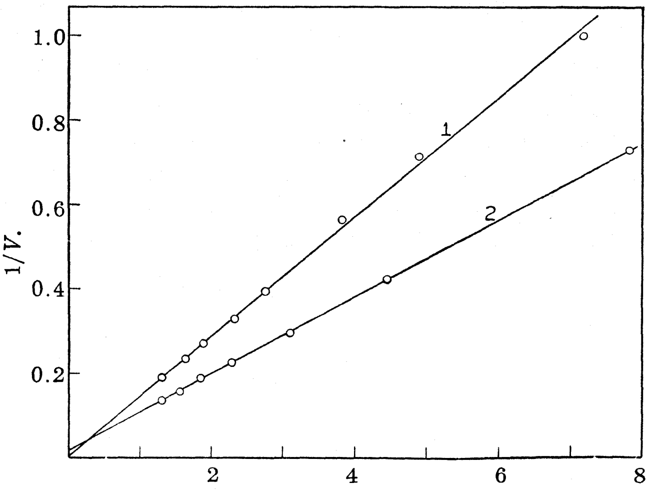

Fig. 3.—Variation of $1/V$ with $1/p$ for the adsorption of oxygen at 100° (Curve 1), and of carbon monoxide at 100° (Curve 2).

Similarly for Gas 2, $\mu_2 = k_2p_2\ (1-\sigma_1-\sigma_2)$ and $\nu_2 = k_2'\sigma_2$. At equilibrium, where the rates of condensation and evaporation are equal

$$k_1p_1\ (1 - \sigma_1 - \sigma_2) = k_1'\sigma_1$$

Substitution of a for k_1/k_1' and simplification gives

$$\sigma_1 = \frac{ap_1\ (1 - \sigma_2)}{1 + ap_1} \tag{2}$$

Similarly for Gas 2

$$\sigma_2 = \frac{bp_2\ (1 - \sigma_1)}{1 + bp_2} \tag{3}$$

Substitution in (2) of the value of σ_2 from **(3)** gives

$$\sigma_1 = \frac{ap_1}{1 + ap_1 + bp_2} \tag{4}$$

and for σ_2

$$\sigma_2 = \frac{bp_2}{1 + ap_1 + bp_2} \tag{5}$$

The fraction of the surface, a, covered by a gas may be expressed by the equation, a = V/V^0, where V and V^0 have the same significance as before. Making the substitutions for σ_1 and σ_2 in Equations 4 and 5, we arrive at the final equations

$$V_1 = \frac{aV_1^\circ p_1}{1 + ap_1 + bp_2} \tag{6}$$

$$V_2 = \frac{bV_2^\circ p_2}{1 + ap_1 + bp_2} \tag{7}$$

Equations 6 and 7 involving constants previously determined from the isotherms ior the separate gases indicate that the presence of a second gas should diminish the amount of the first gas adsorbed, particularly at high pressures of the second gas. From these equations and the constants recorded in Table VXI, the adsorbed volumes have been calculated and recorded in the fifth and eighth columns of Tables III, IV, V, VI.

The values recorded in Table III show that in mixtures of carbon monoxide and oxygen at 0° the adsorption of each gas at given pressure is materially diminished by the presence of the other gas. The amount of oxygen adsorbed, however, is more than the amount calculated from Equations 6 and 7, while the reverse is, in general, the case for carbon monoxide. Table IV shows essentially similar relations for these gases at 100°.

In mixtures of carbon dioxide with oxygen or with carbon monoxide, the adsorption of the dioxide is many times greater than that of the second component. Tables V and VI show that at the higher pressures of carbon dioxide the adsorbed volumes of either oxygen or carbon monoxide are not only greater than the calculated volumes but even exceed the amounts which would be adsorbed in absence of the carbon dioxide. At the lower pressures of the dioxide the adsorbed volumes of oxygen and carbon monoxide are less than the isotherm volumes but greater than the calculated. It is seen that the corresponding comparison is, in general, true with respect to the amount of carbon dioxide adsorbed in these mixtures.

Equations 6 and 7 require that the ratio of the adsorbed volumes should be proportional to the ratio of the pressures of the two gases. Division of (7) by (6) gives the expression

$$\frac{V_2}{V_1} = \frac{bV_2^\circ p_2}{aV_1^\circ p_1}$$

or, since in these experiments $p_2 = 760 - p_1$

$$\frac{V_2}{V_1} = \frac{760bV_2^\circ}{aV_1^\circ p_1} - \frac{bV_2^\circ}{aV_1^\circ} \tag{8}$$

Thus, if V_2/V_1 is plotted against $1/p_1$, the experimental points should lie on a straight line whose slope is $760\ bV_2^\circ/aV_1^\circ$. When plotted in this manner the observed adsorptions in mixtures of carbon monoxide and oxygen at 0 and at 100° agree fairly well with Equation 8. In the case of mixtures containing carbon dioxide, however, the plotted points lie on a distinct curve, which approaches the theoretical straight line at the lower pressures of the dioxide.

The applicability of Equation 7 (or 6) may be tested without employing the constants obtained from the isotherms of the separate gases, by putting it in the form

$$\frac{1}{V_2} = \frac{1 + 760a}{bV_2^\circ p_2} + \frac{b - a}{bV_2^\circ}$$

By plotting $1/V$ against $1/p$ for each gas in each mixture, it was found that the points yield satisfactory straight lines for both components of the carbon monoxide–oxygen mixtures, and for carbon dioxide in mixtures containing this gas. The points for either oxygen or carbon monoxide in mixtures with the dioxide yield distinct curves.

Conclusions

The results of this study show that the assumptions underlying Equations 6 and 7 are fairly satisfactory for mixtures of carbon monoxide and oxygen, but prove inadequate when applied to mixtures containing carbon dioxide. It is apparent that the failure of the equations in the latter case cannot be attributed entirely to the assumptions of unimolecular adsorption and uniformity of surface, since these assumptions are also necessary in deriving Equation 1 for the individual gases, and this equation has been shown to give satisfactory results over the range in question.

It is concluded, therefore, that the failure of Equations 6 and 7 in the case of mixtures containing carbon dioxide is to be attributed mainly to interaction between the adsorbed molecules in the sense that the rate of evaporation of a given molecule may be decreased by the presence in an adjacent space of a molecule of a second gas. Elaboration of this idea may be postponed until further data have been accumulated.

Summary

1. The adsorption of each gas in binary mixtures of carbon monoxide and oxygen has been measured at one atmosphere and temperatures of 0 and 100°, and in mixtures of carbon dioxide with carbon monoxide and with oxygen at 100°. The isotherms of the separate gases have been determined at the same temperatures.

2. The results have been interpreted on the basis of a simple extension of Langmuir's theory of adsorption to the case of gas mixtures. The equations so derived permit the adsorption of each gas in the mixture to be calculated for any given partial pressures without the employment of constants other than those obtainable from the isotherms of the separate gases. The equations indicate that each gas in the mixture should be adsorbed to a smaller extent than if it were present alone at the same partial pressure.

3. With mixtures of carbon monoxide and oxygen there is rough agreement between the calculated and observed adsorptions. On the other

hand, in mixtures containing carbon dioxide the observed values are not only greater than the calculated, but in many cases even exceed the adsorptions found in the absence of the second gas. Pending the accumulation of further data, it is suggested that this anomaly may be due to some kind of mutual interaction between the two kinds of adsorbed molecules.

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

NUCLEAR SPIN AND THE THIRD LAW OF THERMODYNAMICS. THE ENTROPY OF IODINE

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RECEIVED NOVEMBER 29, 1930 PUBLISHED FEBRUARY 9, 1931

Much interest is attached to the problem of determining the manner in which nuclear spin is concerned in the application of the third law of thermodynamics. The somewhat complicated but well-established situation which exists in hydrogen has recently been discussed.[1] In this case nuclear spin results in ortho and para forms which establish equilibrium with each other so slowly that it is impractical to use heat capacity measurements to obtain the entropy. However, it was suggested that hydrogen might be the only substance in which nuclear spin would appreciably affect the calorimetric properties at temperatures above a few degrees absolute. If this proves to be true, it will be convenient to ignore the effect of nuclear spin on the absolute entropy except for hydrogen. This would be possible since, as first pointed out by Gibson and Heitler,[2] for certain gas reactions, the limiting contribution which nuclear spin makes to the entropy cancels in obtaining the entropy change which occurs during a reaction.

The diatomic elements offer a suitable opportunity for obtaining information concerning the above problem and of these the ones consisting primarily of one isotope present the most favorable cases. Diatomic gas molecules which consist of two isotopes of the same element do not have the division of such molecules into ortho and para states. This is the situation most open to suspicion in connection with the possibility of anomalous calorimetric effects. For example, in chlorine the 35–37 molecules would be expected to establish their limiting spin entropy below the lowest attained temperature. The 35–35 and 37–37 molecules are of the type in which we are more interested. Since these latter two would behave differently if the nuclear spins of the two isotopes are different, we believe it best to confine the initial investigation to simpler substances. Of these nitrogen is at present under experimental investigation and existing data on iodine are sufficient for our purpose. In this paper we shall consider the case of iodine.

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[1] Giauque, THIS JOURNAL, 52, 4816 (1930).

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

The nuclear spin of iodine is undetermined but it is known to be large. This is determined from the fact that alternation of intensity in the lines of its band spectrum has not been observed.[3] This is the limiting case approached when the nuclear spin is large. Elements with spins of a few units give an easily observed intensity alternation. However, it can be shown that the limiting nuclear spin entropy has been essentially established at a temperature of 10°K. and presumably much lower even though we are unaware of its exact value.

The available data consist of heat capacity measurements of several observers on solid iodine extending to below 10°K., various vapor pressure determinations and measurements of the band spectrum of diatomic iodine gas.

The Heat Capacity and Entropy of Iodine.—Of the numerous low temperature determinations of the heat capacity of iodine,[4] only the series due to Lange can be given any weight as an accurate piece of work. Lange covered only the range from 9 to 52°K. but fortunately even at 52°K. the heat capacity is rapidly approaching the equipartition value. In extending the curve to room temperature a decision had to be made between data with extreme deviations of as much as 6%. In making this decision the value of $C_p - C_v$, which is known from the following thermodynamic relationship, was of considerable importance.[5]

$$C_p - C_v = \frac{\alpha^2 VT}{\beta}$$

where α and β are the coefficients of expansion and compressibility, respectively. Lewis and Gibson[6] have given the above difference as 0.9 calories/degree per gram atom of iodine at 298.1°K. A repetition of their calculation, using the data given in the "International Critical Tables," raises this somewhat. The value adopted was 1.0 calorie/degree per gram atom at room temperature. When this amount was considered it became evident that the only reasonable C_v curve which could be extended to 298.1°K. passed quite well through the results of Nernst, Koref and Lindemann.[4a]

On calculating the entropy from the above curve a value was obtained which agreed so closely with that given in the "International Critical Tables" by Rodebush and Rodebush[7] that the "International Critical Tables" value was adopted except with regard to the estimate of accuracy.

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[3] For example, see the discussion by Mulliken, *Trans. Faraday Soc.*, 25, 634 (1929).

[4] (a) Nernst, Koref and Lindemann, *Berlin Sitzber.*, 247 (1910); (b) Nernst, *ibid.*, 262 (1910); (c) Nernst, *Ann. Physik.*, [4] **36**, 395 (1911); (d) Gunther, *ibid.*, [4] 51, 828 (1916); (e) Lange, *Z. physik. Chem.*, 110, 343 (1924).

[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 136.

[6] Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917).

[7] Rodebush and Rodebush, "International Critical Tables," Vol. V, p. 88.

We believe that the value of $S_{298.1^\circ\mathrm{K.}} = 27.9$ calorie/degree per mole of solid iodine (I_2) is reliable to 0.1 unit. This value, as will be shown, is not the absolute entropy of iodine, but is, as we shall now assume, the absolute entropy less the unknown amount of the limiting nuclear spin entropy.

The entropy of gaseous iodine may be obtained from the band spectrum for this substance. A summary of the spectroscopic data with references has been given by Birge.[8]

$$S^\circ = \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln P + \frac{5}{2} R - 7.267 + R \ln Q + RT \frac{\mathrm{d} \ln Q}{\mathrm{d}T}{}^{9}$$

where $Q = \Sigma p e^{-\epsilon/kT}$, p is the *a priori* probability and ϵ the energy of the state concerned. The other symbols in the above expression have their usual significance. In evaluating Q the vibrational energies were obtained from the expression

$$\epsilon_v \text{ (in cm.}^{-1}) = 214.26\,(v + \tfrac{1}{2}) - 0.592\,(v + \tfrac{1}{2})^2$$

where $v = 0, 1, 2, 3$, etc. This formula yields the same values as the older type given in "Molecular Spectra in Gases,"[8] but has been converted to the later nomenclature which recognizes the existence of one-half unit of zero point vibration.

In considering the rotation the approximation $Q_r = 4a^2 1kT/h^2$ was sufficiently accurate for our present purpose since the rotational deformation of the iodine molecule is not great. This value of Q_r takes into consideration the fact that the symmetry of the iodine molecule reduces the number of states, and thus Q_r, by a factor of two.

$$I = 742.6 \times 10^{-40} \text{ g. cm.}^2 = \text{the moment of inertia}$$

$$Q = Q_v Q_r = \frac{4\pi^2 IKT}{h^2} \sum_{v=0}^{v} e^{-hc\epsilon_v/kT}$$

The values used for all natural constants are those given in the "International Critical Tables." The rotational approximation leads to

$$RT \frac{\mathrm{d} \ln Q_r}{\mathrm{d}T} = R = 1.9869 \text{ calories/degree per mole}$$

$$RT \frac{\mathrm{d} \ln Q}{\mathrm{d}T} = R\left[T \frac{\mathrm{d} \ln Q_r}{\mathrm{d}T} + T \frac{\mathrm{d} \ln Q_v}{\mathrm{d}T}\right]$$

$$= R\left[1 + \frac{hc}{kT} \frac{\Sigma \epsilon_v e^{-hc\epsilon_v/kT}}{\Sigma e^{-hc\epsilon_v/kT}}\right]$$

From the above we find

$$\begin{aligned} S^\circ_{298.1} &= S_{\mathrm{Translation}} + S_{\mathrm{Rotation}} + S_{\mathrm{Vibration}} \\ &= 42.50 + 17.75 + 2.04 \\ &= 62.29 \text{ calories/degree per mole} \end{aligned}$$

The value 62.29 E. U. is the absolute entropy of iodine *less* the amount due to nuclear spin.

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[8] Birge, "Molecular Spectra in Gases," Bull. Nat. Res. Council, Vol. 11, Part 3, p. 231.

[9] Giauque, THIS JOURNAL, 52,4808 (1930).

The AS for the vaporization of iodine could be calculated from the above data and compared with that found from the vapor pressure data. However, a more severe test of the individual experimental data will be **made.**

The Heat of Vaporization of Iodine

$$F^\circ = H^\circ - TS^\circ$$
$$= E_0^\circ + RT^2 \frac{\mathrm{d}\ in\ Q_v}{\mathrm{d}T} + \frac{7}{2}RT - TS^o$$

where E_0° is the energy content of perfect molecular iodine gas at the absolute zero. From the data given above

$$F^\circ_{298\cdot1} = E_0^\circ + 342 + 3.5 \times 1.9869 \times 298.1 - 298.1 \times 62.29$$
$$= E_0^\circ - 16{,}154 \text{ calories for } I_2 \text{ gas}$$
$$H^\circ_{298} = E_0^\circ + 2415 \text{ calories}$$

From Rodebush and Rodebush[7]

$$F^\circ_{298\cdot1} = E_0^\circ - 5137 \text{ calories for } I_2 \text{ solid}$$
$$H^\circ_{298\cdot1} = E_0^\circ + 3178 \text{ calories}$$

Therefore $\Delta F^\circ_{298\cdot1} = \Delta E_0^\circ - 11{,}017$. With sufficient accuracy the value of $C_{p(g)} - C_{p(s)}$ may be taken as $9.0 - 13.0 = -4.0$ calories/degree per mole between 0 and 100°. Then for the above range $\Delta H_T = \Delta E_0^\circ + 429 - 4.0\ T$

$$\frac{\mathrm{d}(\Delta F/T)}{\mathrm{d}T} = -\frac{\Delta H}{T^2}$$

Evaluating the integration constant from the value of $\Delta F_{298\cdot1}$

$$AF^o = \Delta E_0^\circ + 429 + 4.0\ T \ln T - 61.186\ T$$
$$= -RT \ln P$$

where P is the vapor pressure of iodine in atmospheres. From this equation each measurement of vapor pressure gives a value of ΔE_0°.

The value of ΔE_0° should remain constant if our assumption that the nuclear spin entropy has reached its limiting value below 10°K. is correct.

The results from the data of Baxter, Hickey and Holmes[10] and of Baxter and Grose[11] are given in Table I.

In Table II the earlier and somewhat less accurate data of Ramsay and Young[12] are considered for completeness but are given no weight.

Before proceeding with the main object of this paper, we will pause to obtain a very reliable equation for representing the vapor pressure of solid iodine. Taking $\Delta E_0^\circ = 15{,}640$, we find

$$-RT \ln P \text{ (atm.)} = 16{,}069 + 4.0\ T \ln T - 61.186\ T, \text{ or}$$
$$\log P \text{ (atm.)} = -\frac{3512.3}{T} - 2.013 \log T + 13.374$$

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[10] Baxter, Hickey and Holmes, THIS JOURNAL, 29, 127 (1907)

[11] Baxter and Grose, *ibid.*, 37, 1061 (1915).

[12] Ramsay and Young, J. *Chem. Soc.*, 49,453 (1886).

TABLE I

HEAT OF SUBLIMATION OF IODINE AT THE ABSOLUTE ZERO

Temperature, degrees absolute	Vapor pressure, mm.	ΔE_0° calories per mole	Observers
273.1	0.030	15655	B., H. and H.
288.1	.031	15633	B., H. and H.
298.1	.305	15630	B., H. and H.
303.1	.469	15640	B., H. and H.
308.1	.699	15640	B., H and H.
313.1	1.025	15643	B., H. and H.
318.1	1.498	15639	B., H. and H.
323.1	2.154	15639	B., H. and H
323.1	2.154	15639	B. and G.
328.1	3.084	15633	B., H. and H.
328.1	3.069	15636	B. and G.
333.1	4.285	15647	B. and G.
338.1	5.962	15643	B. and G.
343.1	8.196	15640	B. and G.
348.1	11.21	15637	B. and G.
353.1	15.09	15639	B. and G.
358.1	20.21	15639	B. and G.
363.1	26.78	15640	B. and G.
368.1	35.24	15640	B. and G.

Average 15640 ± 3 calories (av. dev.)

TABLE II

HEAT OF SUBLIMATION OF IODINE AT THE ABSOLUTE ZERO

Data of Ramsay and Young

Temperature, degrees absolute	Vapor pressure, mm.	ΔE_0° calories per mole	Temperature, degrees absolute	Vapor pressure, mm.	calories per mole
331.2	4.9	15467	364.9	28.95	15656
337.6	6.05	15608	365.0	29.6	15644
339.4	6.25	15664	369.9	37.8	15660
348.3	11.5	15628	375.8	50.65	15674
353.5	15.15	15653	378.8	59.85	15665
359.1	21.25	15644	386.9	87.0	15689

An accurate value of $\Delta H_{298.1}$ for the sublimation of iodine may be calculated from

$$\Delta H_T = 15{,}640 + 429 - 4.0\,T$$
$$\Delta H_{298.1} = 14{,}877 \text{ calories per mole}$$

This value is more reliable than the value of ΔE_0°, since any error in the 429 calorie term which appears in the equation does not affect the constancy of the ΔE_0° calculated. However, since the value of ΔE_0° would be shifted by an exactly compensating amount, a reliable value of ΔH is assured. It may be well to add that there is no reason for questioning the reliability of ΔE_0°.

The excellent constancy of ΔE_0° in Table I is a substantial proof of the assumption on which the calculation was based. If, for example, the effect of nuclear spin appeared in the heat capacity measurements above 10°K. to an extent which caused an effect of one entropy unit, a linear trend of about 100 calories would have been evident in ΔE_0°. Thus the data on iodine confirm the idea that the $\int_0^T C_p \mathrm{d} \ln T$ with the usual extrapolation below a few degrees absolute will usually ignore the effect due to nuclear spin. As mentioned above, this is not even approximately true in the case of hydrogen, but this substance is unusual in many ways; for example, unlike all other substances it condenses at temperatures far below those at which the limiting high temperature spin distribution is approached. Since Bonhoeffer and Harteck[13] have shown that the perturbing effects of increased pressure are effective in restoring equilibrium in the case of hydrogen at room temperature, it would be expected that the intimate contact associated with condensation would be even more effective. However, in hydrogen, condensation does not occur until such low temperatures have been reached that the rate has been decreased sufficiently to permit the establishment of a false equilibrium.

In iodine the results indicate that the ortho molecules, which have the rotational quantum numbers $j = 1, 3, 5 \ldots$, do not carry the rotational multiplicity of the lowest ortho state, namely, $p = 2j + 1 = 2 \times 1 + 1 = 3$, into the solid as is the case with hydrogen. However, the results indicate that both para and ortho iodine carry their respective spin multiplicities into the solid state.

We have had many interesting discussions of the above results with Professor Linus Pauling, who has recently[14] given a quantum mechanical discussion of the conditions under which molecules may possess rotational quantum levels in the solid state. Pauling has expressed the difference between the hydrogen and iodine cases as follows: the rotational quanta of the hydrogen molecule involve energies and forces which are large compared to the similar quantities concerned in crystalline hydrogen; thus crystallization is unable to prevent rotational motion. In the case of iodine with its relatively very small rotational quanta and relatively large crystal forces, rotation within the solid becomes impossible.

To illustrate the way in which the third law should be used, we will consider the reaction

$$\begin{aligned} H_2(g) + I_2(s) &= 2HI(g) \\ S_{298\cdot 1},\ HI(g) &= 49.8 \text{ E. U.} \quad S_{298\cdot 1},\ I_2(s) = 27.9 \text{ E. U} \\ S_{298\cdot 1},\ H_2(g) &= 31.23 \text{ E. U.} \\ \Delta S_{298\cdot 1} &= 2 \times 49.8 - 31.23 - 27.9 = 40.5 \end{aligned}$$

In no case is the given entropy value the absolute entropy. In the case of hydrogen the value[8] 31.23 was obtained by reducing the known absolute

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[13] Bonhoeffer and Harteck, *Z. physik. Chem.*, [B] 4, 113 (1929).

[14] Pauling, *Phys. Rev.*, 36, 430 (1930).

entropy by the amount due to the nuclear spin effect. In the case of hydrogen iodide[15] the effect of nuclear spin has not been observed either in the band spectrum or in the low temperature heat capacity measurements and is thus eliminated. For solid iodine we have seen above that the heat capacity with the usual extrapolation at very low temperatures has eliminated the effect of the nuclear spin which it is known to possess. Thus by a simple artifice the cancellation of nuclear spin entropy effect has been accomplished and the correct entropy change during reaction has been obtained.

Were it possible to measure the heat capacity sufficiently close to the absolute zero of temperature, the correct absolute entropy would be obtained but this is not practicable. Thus it appears necessary to make the very plausible assumption that the usual methods of obtaining entropy, while not absolute, for the reasons given above, will lead to correct entropy changes in reactions, except in the case of hydrogen, where the adjusted value given above may be used.

Further investigations are necessary and are being undertaken to find if substances other than hydrogen deviate from the proposed rule.

Summary

The heat capacity, vapor pressure and spectroscopic data on iodine have been used to obtain accurate values for the heat of sublimation and entropy of iodine.

The heat of sublimation of iodine was found to be 15,640 calories per mole at the absolute zero and 14,877 calories per mole at 298.1°K.

With the assistance of the spectroscopic data a reliable equation for the vapor pressure of solid iodine has been obtained.

$$\text{Log}_{10} P \text{ (atm.)} = -\frac{3512.3}{T} - 2.013 \log_{10} T + 13.374$$

$$S_{298.1},\ I_2(s) = 27.9 \pm 0.1 \text{ calories/degree per mole}$$

$$S_{298.1},\ I_2(g) = 62.29 \text{ calories/degree per mole}$$

These quantities are not the absolute entropies of iodine but are less than the absolute entropies by the amount of entropy due to nuclear spin This amount is at present unknown.

The values given can be used in combination with other such values to obtain entropy changes accompanying chemical reactions.

It has been determined that the limiting high temperature entropy effect due to nuclear spin in iodine persists to temperatures below 10°K. This is important since if, as expected, this characteristic proves to be general except for the known exception of hydrogen, it will greatly simplify the complications introduced by nuclear spin in connection with the application of the third law of thermodynamics,

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[15] Giauque and Wiebe, THIS JOURNAL, 51, 1441 (1929).

Although odd and even rotation species exist in diatomic iodine gas, the data show that molecular rotation of the type existing in solid hydrogen does not occur in solid iodine. However, the results indicate that both para and ortho iodine carry their respective spin multiplicities into the solid state.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

PHOTOCHEMICAL STUDIES.
XII. THE PHOTOCHEMICAL REACTION BETWEEN NITRIC OXIDE AND MERCURY VAPOR

BY W. ALBERT NOYES, JR.

RECEIVED NOVEMBER 29, 1930 PUBLISHED FEBRUARY 9, 1931

The field of investigation initiated by the fundamental researches of Cario[1] and of Cario and Franck,[2] in which the spectra of thallium and of silver and the dissociation of hydrogen were produced through the agency of excited mercury atoms, has proved to be of great theoretical interest. These phenomena, ascribed to inelastic collisions of the second kind, have been shown to be quite universal and have been demonstrated for a large variety of reactions by many different workers. It is not necessary at this point to give a detailed list of such reactions.[3]

The exact mechanism of such photosensitized reactions is of some interest. The various experimental facts and theoretical ideas concerning the action of excited mercury on hydrogen and water vapor have been summarized and discussed recently by Beutler and Rabinowitsch.[4] The production of ozone from oxygen, first studied by Dickinson and Sherrill,[5] has been investigated from different angles by other investigators.[6] Various mechanisms have been proposed to account for this reaction[7] and among others one which depends, essentially, on the fact that oxygen is paramagnetic. It was with the object of throwing further light upon the mechanisms of some types of photosensitization that the present investigation, involving also the action of excited mercury on a paramagnetic gas, nitric oxide, was undertaken.

[1] Cario, *Z. Physik*, 10, 185 (1922).

[2] Cario and Franck, *ibid.*, 11, 161 (1922).

[3] For a recent summary see Griffith and McKeown, "Photo-processes in Gaseous and Liquid Systems," Longmans, Green and Co., London, 1929, p. 582 *et seq.*

[4] Beutler and Rabinowitsch, *Z. physik. Chem.*, 8B, 403 (1930).

[5] Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, 12, 175 (1926).

[6] Noyes, THIS JOURNAL, 49, 3100 (1927); Leipunsky and Sagulin, *Z physik. Chem.*, 1B, 362 (1928); 3B, 215 (1929); Noyes, *ibid.*, 2B, 445 (1929).

[7] See also Gaviola, *Phys. Rev.*, 33, 309 (1929).

I. Experimental

The nitric oxide used in these experiments was prepared by the method of Winkler,[8] introducing some of the modifications suggested by Johnston and Giauque.[9] This method is based upon the reaction: $2NO_2^- + 4H^+ + 2I^- = 2NO + I_2 + 2H_2O$. The flask C (Fig 1) was partially filled with a solution made by dissolving *75* g. of potassium nitrite and **38** g. of potassium iodide in **225** cc. of distilled water. The flask **A** contained a 50% (by weight) solution of sulfuric acid. The column D was filled with glass beads and contained concentrated sulfuric acid (about 93%). The column ***G*** also contained glass beads and was filled with a 50% solution of potassium hydroxide. The flask T served merely as a protective trap in case of accident. *J* contained anhydrous calcium chloride for removing most of the moisture and K contained phosphorus pentoxide.

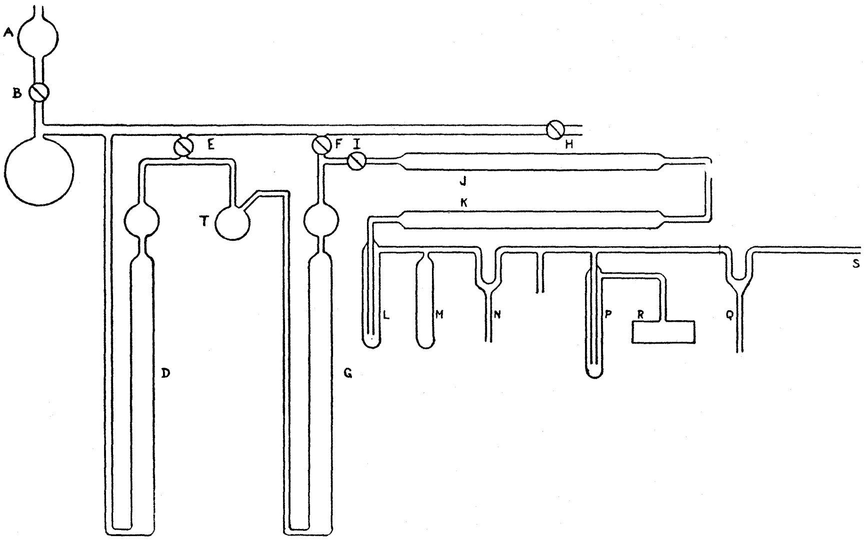

Fig. 1.

The stopcock I was closed and the mercury in cut-offs N and Q was lowered. The entire apparatus as far as I was then evacuated with continual flaming to as low **a** pressure as could be obtained with a mercury diffusion pump. The stopcocks E and F were then opened and the gas preparation apparatus was evacuated through H by means of an oil pump. This evacuation was carried on until a low pressure was attained, limited largely by the vapor pressure of water over the solution in C. In this way practically all of the air in the gas phase and a large fraction of the air dissolved in the various solutions was eliminated. Stopcocks E, F and H were closed and a few drops of the sulfuric acid solution allowed to enter C through the stopcock B. The gas evolved bubbled through the 75-cm. column of sulfuric acid in D and then through the concentrated potassium hydroxide in G. Stopcocks E, F and H were opened and the gas pumped out. This process was repeated at least twice before gas was admitted to the main apparatus. Finally stopcocks E, F and H were closed and I opened. Nitric oxide was allowed to flow through the calcium chloride and phosphorus pentoxide tubes

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[8] Winkler, *Ber.*, 34, **1408 (1901).**

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

for several minutes and then the mercury in the cut-off N was raised and liquid air was placed around the trap L. When sufficient nitric oxide had collected in L the stopcock I was closed. The amount of nitric oxide prepared was never large, usually only sufficient to exert about five centimeters pressure when the liquid air was removed from L. The liquid air was now removed from L and placed around M and the nitric oxide sublimed over. The last fraction was allowed to escape by lowering the mercury in N with the vacuum pumps attached to S in operation. This process of purification by sublimation was repeated at least three times before using any nitric oxide for an experiment.

The nitric oxide as it leaves C would contain as impurities some hydriodic acid, traces of nitrogen and iodine and unknown amounts of other oxides of nitrogen (with perhaps a small amount of free oxygen). The hydriodic acid is probably partially removed by the sulfuric acid. Passage of the gas through the concentrated potassium hydroxide should remove most of the iodine, the remaining traces of hydriodic acid and nitrogen dioxide. The only nitrogen oxide not accounted for would be N_2O, although this would probably not be formed in any appreciable quantity. It is quite soluble in water but probably would not be completely removed. The repeated distillations with liquid air would tend to eliminate practically all of the highly volatile impurities such as nitrogen and oxygen completely. The others, namely, hydriodic acid and the various foreign oxides of nitrogen, would have exceedingly low vapor pressures at the temperature of liquid air. They would probably not be removed completely by the distillation process.

The vapor pressure[9] of nitric oxide at the temperature of boiling oxygen (90.13° K.)[10] is about 3.2 mm. and at the temperature of boiling nitrogen it is about 0.1 mm.[11] In most of the experiments described in the present paper, the pressure of nitric oxide used was not greater than 0.15 mm., so that the gas could be admitted to the reaction vessel from a trap immersed in liquid air. In these experiments the only possible volatile impurities were nitrogen and oxygen. These were swept away as far as possible by submitting the solid at liquid-air temperatures to a high vacuum, as well as by the process of sublimation already described. When pressures of several millimeters of nitric oxide were necessary, the liquid air was removed from the trap L and the gas coming off allowed to bubble through about one centimeter of mercury in the cut-off N. This would tend to remove those oxides of nitrogen which react readily with mercury and would also make it possible to use only the first portion of gas coming off from the solid. Since nitric oxide is much more volatile than any of the impurities (other than nitrogen and oxygen), this method should ensure a high purity of the gas used.

The pressures were all measured by means of a McLeod gage.

The reaction vessel was of fused quartz, *25* mm. in diameter and 48 mm. in length. It was sealed to the vacuum line by a graded quartz to pyrex seal. No stopcocks or other sources of organic impurities were present in the line between the two cut-offs N and Q. The admission of gas to the line while L was immersed in liquid air should ensure absence of organic vapors as impurities. In certain of the later experiments a reaction vessel made of Corex glass was used. This glass may be sealed directly to pyrex.

The quartz mercury arc lamp and the reaction vessel were both immersed in a water-bath. The distance from the lamp to the window of the reaction vessel was negligible. The current through the lamp was supplied by a motor generator. The variations between runs is to be ascribed undoubtedly to variations in voltage of the line supplying the lamp.

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[10] Giauque and Johnston, THIS JOURNAL, 51, 2313 (1929).

[11] Calculated from the formula given by Giauque and Johnston,[9] although their data did not extend to such low temperatures.

II. Results

The first object of the experiments was to determine the effect of pressure of nitric oxide on the rate of the reaction. In the reaction of excited mercury with oxygen,[5,6] a film of mercuric oxide was produced on the side of the reaction vessel toward the source of radiation. In the present experiments no such film was noticed.

It seems evident that the gas remaining in the reaction vessel after the completion of the reaction is nitrogen. This is rendered reasonable by the fact that the final pressure attained after very long exposure is always, very close to one-half the initial pressure. That conditions are actually not quite as simple as this is indicated by the variation in pressure, both with and without illumination, after the pressure had attained approximately one-half the initial value. With continuous illumination the pressure would decrease to a value less than one-half the initial pressure, but on standing there would be a gradual pressure increase. It seemed impossible, however, to repeat this process indefinitely, for sooner or later the pressure decrease during illumination would cease and the pressure would gradually increase with or without illumination. Every precaution was taken to be sure that this increase was not due to a leak in the apparatus.

The reaction seems to lead to the production of nitrogen dioxide. The action of this gas on liquid mercury has been studied previously.[12] It is not exceedingly rapid at low pressures. The final reaction is supposed to be represented by the equation[13] $4Hg + 2NO_2 = 4HgO + N_2$, but the initial step is almost certainly the formation of a mercuric or mercurous salt, perhaps a nitrite, which may then evolve nitrogen more slowly.

TABLE I

RESULTS OF A TYPICAL RUN

Reaction vessel, quartz. Current, 5.8 amp. Temp., 25°

Time, min.	Pressure, mm.	Pressure (calcd.), mm.
0	0.0339	(0.0339)
55	.0307	.0299
213	.0229	.0224
303	.0206	.0208
968	.0171	.0171

Table I shows the results obtained during a typical run. The values in the third column are calculated by means of the equation

$$(2.303/t) \log_{10} (p_0 - {}^1/_2\, p_0)/(p - {}^1/_2\, p_0) = 4.91 \cdot 10^{-3} \qquad (1)$$

Many other runs were made and in all cases the reaction rate followed the equation

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[12] Moore and Noyes, THIS JOURNAL, 46, *1367 (1924);* Moore, *ibid.*, *47, 2932 (1925);* Noyes, *Trans. Faraday Soc.*, *21, 569 (1926);* Pierce and Noyes, THIS JOURNAL, 50, *2179 (1928).*

[13] "Watts' Dictionary of Chemistry," Longmans, Green and Co., London, 1894, Vol. III, p. 566.

$$-dp/dt = k_1 (p - {}^1/_2\, p_0) \qquad (2)$$

within the experimental error, p_0 being the initial pressure and p the pressure at the time t. Table II shows a typical run with Corex glass.

TABLE II

TYPICAL RUN WITH COREX GLASS

Reaction vessel, Corex. Current, 6.3 amp. Temp., 25°. $k_1 = 1.45 \cdot 10^{-4}$

Time, min.	Pressure, mm.	Pressure (calcd.), mm.
0	0.1285	0.1285
175	.1260	.1270
950	.1199	.1203
1660	.1148	.1148

In order to determine the possible effect of pressure on the values of the constant, k_1, a series of runs was made at varying pressures with other conditions identical as nearly as possible. Nitric oxide from the same preparation was used and the runs followed each other as closely as possible Table III shows the results obtained.

TABLE III

EXPERIMENTAL DATA

Time interval, min.	Initial pressure, mm.	Final pressure, mm.	Current, amp.	k_1
31	0.1178	0.1128	6.2	$2.9 \cdot 10^{-3}$
30	.0340	.0330	6.1	2.0
30	.00353	.00338	6.0	3.1

Similar series were made on two other occasions with results which showed no systematic variation of k_1 with pressure.

In order to ascertain whether the reaction was really due to the action of excited mercury, or whether it should not be ascribed either to some foreign gas acting as sensitizer or to direct photochemical decomposition of the nitric oxide, the trap P was, during several runs, immersed either in liquid ammonia (−33°) or in liquid air. Constants obtained under these conditions were uniformly much lower, in some cases being actually zero. The fact that the zero value was not always obtained is undoubtedly due to the insufficient time allowed for the complete removal of mercury vapor. In one case in which liquid air had no apparent effect, close examination showed mercury droplets to be present in the reaction vessel. These had undoubtedly been placed there in the process of flaming the line before the run. Table IV shows a summary of the constants obtained under various conditions.

One run was made at considerably higher pressures of nitric oxide. The initial pressure was 24.13 mm., the time three hours and the final pressure 23.37 mm., giving a value for k_1 of $3.7 \cdot 10^{-4}$. This indicates, as would be expected, that k_1 decreases with pressure. An experiment was made with the same nitric oxide after evacuating the line to a lower pressure. In this

TABLE IV

SUMMARY OF REACTION RATE CONSTANTS

Experimental conditions	k_1 (min.$^{-1}$)
Quartz vessel	$4.7\cdot10^{-3}$
Quartz vessel, *liq.* NH_3 *on P*	0.8
Quartz vessel, liq. *air on P*	.4
Cores vessel	$2.1\cdot10^{-4}$
Corex vessel, liq. *air* on *P*	0.35

way the presence of inhibiting impurities due to the preparation at higher pressures (see Sec. I) would be detected. A value of $4\cdot10^{-3}$ for k_1 was obtained, indicating that the rate was the same as for other lots of nitric oxide.

An attempt was made to determine the percentage transmission of the Corex glass for a wave length of 2536 Å. An average of four determinations gave 0.038 as the ratio of this radiation transmitted by Corex to that transmitted by quartz. That is, an exposure of about five seconds with quartz gave about the same darkening of the plate as an exposure of one hundred and thirty seconds with Corex. The experimental arrangement used in the study of the fluorescence of this line was used. This value should be considered as approximate. An attempt to make the measurement with a rotating sector gave even less reliable results due to the feeble transmission.

The experiments with Corex were carried out with a slightly higher average current through the mercury arc lamp than those with the quartz vessel. The ratio of rates (Corex/Quartz) as given in Table IV is 0.045, which should be considered as too high rather than too low. The square root of 0.038 is 0.19 and the square is 0.0014. Both of these values are considerably removed from 0.045, so that we feel safe in stating that the rate is proportional to the intensity of the resonance radiation.

Studies were also made of the quenching of the fluorescence of mercury vapor by nitric oxide. The apparatus shown schematically in Fig. 2 was used. A is a mercury arc lamp of the vertical type with the lower part immersed in water kept at room temperature. B is a quartz lens and C is the fluorescence tube, approximately 80 cm. in length and tapered and bent over at the end to reduce back reflection in the manner described by Hughes and Thomas.[14] The slit of the spectrograph is shown at D. The various parts of the apparatus were placed in such a manner that radiation was not directly reflected into the spectrograph.

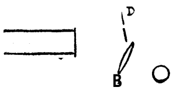

Fig. 2.

With short exposures (up to about one minute) the 2536 Å. line of mercury alone was shown on the photographic plate. With exposures of several minutes a few other lines could be detected, but especially those at 3132, 3654, 4046, 4358 and 5461 Å. These lines are denoted as ($3^3D_1 \longrightarrow 2^3P_2$), ($3^3D_2 \longrightarrow 2^3P_2$), ($2^3S_1 \longrightarrow 2P_0$), ($2^3S_1 \longrightarrow 2^3P_1$) and ($2^3S_1 \longrightarrow 2^3P_2$),

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[14] Hughes *and Thomas,* Phys. *Rev., 30,*466 (1927).

respectively, all of which have initial energy levels which may be produced from the excited state (2^3P_1) by the absorption of lines emitted by the mercury arc. It seems safe to say that very little, if any, reflected radiation need be considered in interpreting these experiments. We assume, therefore, that the intensity of the 2536 Å. as indicated by the spectrograph is proportional to the intensity of the fluorescence.

In determining the extent to which nitric oxide quenches the fluorescence of mercury vapor, exposures were made of five seconds' duration at intervals of one centimeter on the photographic plate with mercury vapor in the fluorescence tube in a high vacuum. Nitric oxide was then admitted and exposures of 5, 10, 15, etc., seconds were made in such a way that they alternated on the photographic plate with those without nitric oxide. Visual comparison was used to ascertain equality of intensity. The average of three plates showed that thirty-three seconds with nitric oxide at a pressure of 6.1 mm. gave the same blackening of the plate as five seconds without. With 2.0 mm. of nitric oxide the ratio was 18/5. Hydrogen was used as a comparison. The hydrogen was not specially purified except by passage through a liquid-air trap. With 6.0 mm. of hydrogen the ratio found was 100/5.

III. Theoretical

The present work was undertaken because nitric oxide is a paramagnetic gas. All, or nearly all, of the homogeneous gas reactions which have been proved definitely to be of the third order, involve nitric oxide.[15] This may indicate that the paramagnetic character of these molecules renders reactions involving triple collisions more probable than for ordinary gases. Hinshelwood[15] has summarized arguments against the existence of N_2O_2 as a definite intermediate.

The line spectrum of mercury has been quite satisfactorily analyzed.[16] The normal state is designated as $^1S_0$, with no resultant electron spin to be ascribed to the kernel and the two valence electrons (s electrons) with their spins antiparallel, giving a resultant of zero. This state, then, should be essentially nonmagnetic. The resonance line (2536 Å.) involves in absorption a $^1S_0 \longrightarrow {}^3P_1$ transition. In the triplet state produced when mercury vapor absorbs this radiation, the electron spins are parallel instead of antiparallel and the atom as a whole now possesses a net electronic orbital angular momentum. This should mean that excited mercury is paramagnetic. Further details concerning the mercury spectrum need not be given here.

The spectrum of nitric oxide has received a great deal of attention. The

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[15] Hinshelwood, *Chem. Reviews*, 3, 237 (1926).

[16] See, for example, Grotrian, "Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei und drei Valenzelektronen," Julius Springer, Berlin, 1928, Vol. II, p. 78.

nitric oxide molecule contains an odd number of electrons and the normal state is a $^2\Pi_{1/2,\,3/2}$ state. For reasons which need not be given here[17] the $^2\Pi_{1/2}$ state will be nearly non-magnetic for small values of the resultant quantum number J, while the $^2\Pi_{3/2}$ state will be paramagnetic. The works of Sponer,[18] Sponer and Hopfield,[19] Jenkins, Barton and Mulliken,[20] Guillery[21] and Schmid[22] have shown that the β, γ and δ bands in all probability have as the same final state the normal $^2\Pi$ state. The upper states seem to be best described as $^2\Sigma$, $^2\Pi$ and $^2\Sigma$ states, respectively.[23] In addition to the normal doublets, NO shows X-type doubling.[24]

The various electron energy levels for NO are given as follows:[23]

X level	($^2\Pi$)	0 volt
A	($^2\Sigma$)	5.45 volts
B	($^2\Pi$)	5.60 volts
C	($^2\Sigma$)	6.45 volts
D	($^2\Sigma$)	6.58 volts

The β, γ and δ band systems (X-B, X-A, X-C, resp.), extend from about 2250 Å. toward shorter wave lengths. Since all of these bands have the normal $^2\Pi$ state as the final state in emission, they should also be observed in absorption. In the experiments described in the present paper, the absorption should be exceedingly feeble, both on account of the low pressures used and because of the fact that a cooled mercury arc lamp gives practically no continuous emission in this region. In view of the results obtained at higher pressures and the fact that the elimination of mercury vapor by liquid air practically stops the reaction, direct absorption of radiation by nitric oxide would seem to be unimportant in the present work.

Mulliken[23] has concluded that the normal $^2\Pi$ state of nitric oxide should separate adiabatically into a normal oxygen atom (^3P) and a normal nitrogen atom (^4S) at the convergence limit of its vibration levels. He gives the value of 7.9 volts for the energy of dissociation. This value is certainly subject to a large uncertainty. The heat of dissociation of nitrogen is fixed at a probable value corresponding to 9–9.5 volts,[25] while that of oxygen is subject to an even greater uncertainty,[26] but may be placed between the

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[17] Van Vleck, *Phys. Rev.*, 31, 608 (1928).

[18] Sponer, *Nature*, **117**, 81 (1926).

[19] Sponer and Hopfield, *Phys. Rev.*, 27,640 (1926).

[20] Jenkins, Barton and Mulliken, *ibid.*, 30, 150 (1927).

[21] Guillery, *Z. Physik*, 42, 121 (1927).

[22] Schmid, *ibid.*, 59, 42 (1929); 64,279 (1930).

[23] Birge and Sponer, *Phys. Rev.*, 28, 259 (1926); Mulliken, *ibid.*, 32, 186, 761 (1928); Chem. *Reviews*, 6, 524 (1929).

[24] Mulliken, *Phys. Rev.*, 33, 508 (1929).

[25] Birge, *ibid.*, 34, 1062 (1929).

[26] Birge and Sponer, *ibid.*, 28, 267 (1926); Herzberg, *Z. physik. Chem.*, 4B, 223 (1929); Copeland, THIS JOURNAL, 52, 2581 (1930); Rodebush and Troxel, *ibid.*, 52, 3467 (1930); Sommer, *Naturwissenschaften*, 18, 752 (1930); Herzberg, *Z. physik. Chem.*. 10B, 189 (1930).

limits of **5.1** and 7 volts, with the probability that the correct value is near the lower limit. The heat of formation of nitric oxide from the elements corresponds to 0.94 volt.[27] We may now set up the following relationships:

$$\begin{array}{lll} NO = {}^1/_2\,N_P + {}^1/_2\,O_2; & AE = +0.94\text{ v.} & \\ {}^1/_2\,N_2 = N; & AE = -4.5\text{ to }-4.75\text{ v.} & \\ {}^1/_2\,O_2 = O; & AE = -2.55\text{ to }-3.5\text{ v.} & \\ \hline NO = N + O; & \Delta E = -6.1\text{ to }-7.3\text{ v.} & (3) \end{array}$$

Since the minimum energy of dissociation of nitric oxide exceeds the 4.9 volt energy of excitation of 2^3P_1 state of mercury by **1.2** volts, the reaction

$$Hg\ (2^3P_1) + NO = Hg\ (1^1S_0) + N + O \qquad (4)$$

may be considered as impossible. However, if the heat of vaporization of mercury is taken as equivalent to 0.55 volt, the heat of formation of mercuric oxide from the elements as 0.93 volt, the reaction

$$Hg\ (2^3P_1) + NO = HgO + N \qquad (5)$$

is found to be exoenergetic to the extent of **2.6** to **2.8** volts. This value is too large by an amount corresponding to the heat of sublimation of mercuric oxide. The latter is not known but certainly should not exceed one volt. Reaction 5 should, therefore, be considered as thermodynamically possible.

Two other possible primary steps may be considered: **(1)** that represented by the equation

$$Hg\ (2^3P_1\text{ or }2^3P_0) + NO = NO^{\circ} + Hg\ (1^1S_0) \qquad (6)$$

where NO° represents an excited nitric oxide molecule. Since the lowest excited electron level of nitric oxide lies 5.45 volts above the normal, NO° would, in all probability, represent a molecule in the normal electron level but in a high vibration-rotation state. **(2)** An excited or metastable mercury atom may stay associated with a nitric oxide molecule a sufficient length of time to render the equivalent of a triple collision possible. The reaction could then be represented by

$$Hg^{\circ} + 2N0 = N_2 + 20 + Hg \qquad (7)$$

or some other reaction of this general type.

The effect of various gases in quenching the fluorescence of mercury vapor has been the subject of several recent investigations.[28,29,30] The quenching may be ascribed to three different types of process: **(1)** loss of energy by the mercury atom due to a simple collision of the second kind with the production of a normal 1^1S_0 atom. This probably occurs when the spectra of thallium and of silver are produced.' **(2)** A definite chemical reaction

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[27] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 560.

[28] Stuart, *Z. Physik*, 32, 262 (1925).

[29] Gaviola, *Phys. Rev.*, 33, 309; 34, 1049, 1373 (1929); 35, 1226 (1930)

[30] Zemansky, *ibid.*, 31, 812 (1928); 36, 919. 219 (1930).

may take place. This may be the case with oxygen and hydrogen.[31] (3) Loss of only a small amount of energy (0.218 volt) with the production of a 2^3P_0 mercury atom. This small amount of energy may appear as energy of vibration and rotation of the quenching molecule. Using the ideas of Kallmann and London,[32] Zemansky[30] has shown that quenching is most apt to occur by this mechanism when the quenching molecule has a vibration level differing from the normal by approximately $(0.218 + {}^1/_2\, kT)$ volt. This process is of importance for such molecules as CH_4, H_2O, CO, CO_2 and N_2.

The first vibration level of nitric oxide lies 0.231 volt above the zero vibration level.[33] This differs from 0.218 volt by 0.013 volt and, according to Zemansky,[30] this should mean that NO would have an exceedingly large "effective cross section for quenching." In fact the cross section should be larger than for any gas given in his diagram.

In the experiments described above, nitric oxide was shown to quench the resonance radiation of mercury to the extent of 72% at a pressure of 2 mm. and 85% at 6 mm. The method used was not capable of the highest precision; moreover the optical arrangement was different from that used by Zemansky,[30] so that a direct comparison with other gases is impossible. A rough calculation shows that the effective cross section for quenching is approximately $2 \cdot 10^{-16}$ sq. cm., not as high as for NH_3, C_4H_{10}, CO and CO_2, but larger than for H_2O, C_2H_6, CH_4 and N_2. The pressure for half quenching would be slightly less than one millimeter, which is lower than the values for other gases studied by Stuart[2*] with the exception of H_2, O_2 and CO. Hydrogen used in the same apparatus showed a quenching of 95%, which agrees within about 1% with the value calculated by the method of Gaviola.[29]

If the quenching in nitric oxide is due to $2^3P_1 \longrightarrow 2^3P_0$ transitions, at higher temperatures the quenching should be noticeably less because there are more collisions capable of causing the reverse process.[34] This experiment was tried, using a cell made entirely of fused quartz. There was much more scattering in this cell than in the one used previously. After proper corrections the results at room temperature agreed fairly satisfactorily with those obtained with the other cell. At a temperature of from 600 to 700°, 7 mm. of nitric oxide gave approximately 10% less

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[31] *Cf.* Zemansky, Ref. 30. A slight error seems to have crept into his consideration of the possibility of the reaction $Hg^0 + O_2 = HgO + O$. This reaction should be exoenergetic to the extent of about 3 volts, a value which is in error by an amount corresponding to the heat of sublimation of mercuric oxide. For other arguments against this mechanism see Dickinson and Sherrill, Ref. 5 and Noyes, Ref 6.

[32] Kallmann and London, *Z. physik.* Chem , 2B, 207 (1929)

[33] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol V, p. 415.

[34] See Cario and Franck, *Z. Physik,* 17, 202 (1923)

quenching than at room temperature. This is an average value obtained in seven different runs. At similar temperatures Cario and Franck[34] found nitrogen to be practically without effect in quenching the fluorescence of mercury vapor. Due to the possibility of introducing impurities it was not advisable to try high pressures of nitric oxide and there is, therefore, the probability that part of the 2^3P_0 atoms are removed by the walls. Moreover nitric oxide quenches the fluorescence of mercury vapor much more effectively than nitrogen. It is questionable whether the quenching should become zero at the temperatures used even if it were due entirely to the production of 2^3P_0 atoms. For reasons to be given later it seems certain that this mechanism is not the only one, but the results do not disprove the presence of some collisions of this type. In fact it seems probable that part of the quenching is to be ascribed to the production of 2^3P_0 atoms.

At 25° the following distribution of nitric oxide molecules among the various vibration states is obtained[35] (neglecting A-type doubling)

$^2\Pi_{1/2}$	$v = 0$	65.04%
$^2\Pi_{1/2}$	$v = 1$	0.477%
$^2\Pi_{1/2}$	$v = 2$	0.004%
$^2\Pi_{3/2}$	$v = 0$	34.23%
$^2\Pi_{3/2}$	$v = 1$	0.250%
$^2\Pi_{3/2}$	$v = 2$	0 0021%

Thus a small but definite fraction of the molecules have a vibrational quantum number of 1. If the majority of the quenching is ascribed to the process NO ($^2\Pi$, $v = 0$) + Hg (2^3P_1) = NO ($^2\Pi$, $v = 1$) + Hg (2^3P_0), certain of the facts presented above may be tentatively explained. At low pressures the 2^3P_0 atoms would diffuse largely to the walls and be converted to normal atoms. As the pressure is increased, the chance for reversal of the above process before the metastable atoms reached the walls would be increased. Thus the quenching at higher pressures could not be calculated by a simple formula from that at low pressures. This would be independent of any effect due to broadening of the absorption line, etc. The qualitative results presented above indicate this to be the case. The lower quenching at higher temperatures could also be explained in this manner.

It is impossible, however, to assume that nitric oxide molecules with a vibrational quantum number of 1 are appreciably more reactive than those with $v = 0$. Otherwise reaction would take place at room temperature and would have a very high temperature coefficient. There must, therefore, be some other process involved.

The 26th vibration level of nitric oxide lies 4.90 volts above the zero level and the 24th is found at 4.61 volts.[36] In optical absorption the forma-

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[35] See Ref. 9, p 3212.

[36] See Ref 33. This value is calculated by means of the formula $\bar{\nu} = v(\omega'' - \omega''x''v)$, where 5 is the vibrational energy in cm.$^{-1}$ and v is the vibrational quantum number. w'' and $\omega''x''$ are constants, 1888.31 and 13.88, respectively. It is recognized that use of

tion of such high levels would be an exceedingly rare occurrence. One might expect their formation by collision of the second kind with 2^3P_1 (4.863 v.) and 2^3P_0 (4.645 v.) mercury atoms to be improbable in the absence of some special resonance effect. The first excited electron level of nitric oxide lies 5.45 volts above the normal and differs from 4.863 volts by an amount probably too large to be of importance in such an effect. However, 5.45 volts is only 5.22, 4.99 and 4.77 volts above the first, second and third vibration levels, respectively. One might expect, therefore, that molecules in vibration levels higher than the zero level would have some possibility of being excited to vibration levels as high as the 26th or 27th. Thus 4.81 volts will raise the first vibration level to the 27th and this differs by only 0.05 volt from the energy 2^3P_1 mercury atoms may give up. Calculations concerning this type of collision may only be made by approximate methods, but is it possible that the paramagnetic characters of the two bodies entering into the collision might be a determining factor in the type of resonance effect obtained?

There are two arguments against the mechanism represented by Equation 5. (1) Mercuric oxide is not deposited in the reaction vessel in the zone of illumination. (2) No bands could be detected which might be ascribed to either HgO or HgN molecules. This last argument should be given little weight since bands, if emitted, might lie in the infra-red. In the absence of a radiative process, such an exoenergetic mechanism would be improbable. Equation 5 would, however, satisfy the rate equations obtained.

Reaction 7 would seem to be excluded by the fact that only the first power of the nitric oxide pressure occurs in the rate equation. Other information concerning this mechanism is lacking.

It seems probable, therefore, that the mechanism is correctly represented by Equation 6. In order for this to be true, the life of NO^0 must be appreciably longer than the average time between collisions even at low pressures. From what is known of the life of molecules in high vibration states, this would not be unexpected.

It can now be shown that the rate of activation of nitric oxide should be given by the equation

$$+\,d(NO^\circ)/dt = c_1c_2Ip/(c_1c_2p + c_3) \qquad (8)$$

(NO°) = total number of activated molecules
I = number of quanta of resonance radiation absorbed per second
p = pressure of nitric oxide in millimeters
c_1 = number of collisions per second per excited mercury atom at 1 mm. pressure
c_2 = fraction of these collisions which lead to activation
$c_3 = 9.7\cdot10^6$ = constant for fluorescent decay of excited mercury

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this formula for such high values of v is approximate, for higher powers of v should undoubtedly be included, Comparison of the rate obtained at low pressures with the one obtained at 24 mm. shows that $c_1c_2 = 5\cdot10.^6$ Equation 8 satisfies all of the requirements of the data presented above, for at low pressures c_1c_2p will be small compared to c_3.

It is impossible to calculate c_1 and c_2 separately without introducing special assumptions. If c~ = 1, the radius of the nitric oxide molecule is found to exceed the kinetic theory radius by a small amount if the radius of the excited mercury atom is taken equal to the kinetic theory radius of the normal mercury atom. If nitric oxide molecules in vibration levels above the lowest are alone capable of reacting, their effective radius would be found to be much larger.

Equation **8** with the values of the various constants determined from reaction rate data gives lower values for the quenching of the fluorescence of mercury vapor than those found experimentally. Thus quenching should be 51% at **2** mm. and 75% at 6 mm. as compared to 72 and **85%** found experimentally. One would not expect precise agreement, however, due to the difference in optical arrangement between the reaction system and that used for the study of fluorescence, as well as on account of certain factors mentioned by Zemansky.[30] This is partial evidence that part of the quenching occurs by a process which does not lead to chemical reaction, presumably through the production of 2^3P_0 atoms.

Summary

1. The rate of pressure decrease in a system consisting of mercury vapor and nitric oxide illuminated with the resonance radiation of mercury has been studied.
2. The quenching of the fluorescence of mercury vapor by nitric oxide has been studied. It is probably to be ascribed to two processes.
3. Various mechanisms for the activation process are discussed. Probably a nitric oxide molecule in a high vibration state of the normal electron level is produced by collisions of the second kind.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. I. THE ETHYL ESTERS OF MONO- AND DICARBOXYLIC ACIDS

BY C. P. SMYTH AND W. S. WALLS

RECEIVED DECEMBER 3, 1930 PUBLISHED FEBRUARY 9, 1931

A series of ten papers has been published from this Laboratory under the general title, "The Dielectric Polarization of Liquids,"[1] but, the applicability of the Debye theory to liquids having been definitely established, dielectric investigations can now safely aim more directly at the problems of electric moment and molecular structure, some of which received preliminary treatment in earlier studies.[2]

Although it was obvious that the complexity of the carboxyl group would complicate the interpretation of the results, the ethyl esters of the dicarboxylic acids appeared to offer a means of investigating the effect upon the resultant electric moment of separating the component moments by a carbon chain of varying length. As this moment is the resultant of the moments of two $—COOC_2H_5$ groups, it seemed desirable to give this group more thorough investigation than it had hitherto received by measuring the ethyl esters of formic, acetic and propionic acids.

The dielectric constants of these substances in solution in benzene were measured by means of a heterodyne beat apparatus similar to those employed by several other investigators,[3] the wave length used being 1000 meters. As previous work[4] had shown that the values of large moments obtained from the temperature variation of the polarization did not differ greatly from those calculated from the difference between the polarization at one temperature and the molar refraction, the measurements were carried out at 25° and repeated at 50° as a means of ascertaining the presence of any complicating factors which would vary with temperature. The cell used to contain the liquid to be measured consisted of concentric gold-plated brass cylinders similar to those used in earlier measurements.[5] An Ostwald–Sprengel pycnometer fitted with carefully ground caps was used for the density measurements. The temperatures were maintained by means of two accurately adjusted thermostats. The refractive indices were measured with a Pulfrich refractometer at 25° for the calculation of the molar refraction and at 20° for comparison with the values contained in the literature, this comparison serving as a means of checking the purity of the materials.

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[1] Smyth and co-workers, THIS JOURNAL, 50, 1536, 1547, 1883 (1928); 51, 1736, 2051,3312,3330 (1929); 52,1824,2227,3546 (1930).

[2] Smyth and co-workers, *Phil.* Mag., 45, 849 (1923); 47, 530 (1924); THIS JOURNAL, 46,2151 (1924); 47,1894,2501 (1925); 49,1030 (1927).

[3] *See* Williams, *Fortschritte Chem., Physik physik. Chem.,* 20, No. 5 (1930).

[4] See Smyth, THIS JOURNAL, 51,2051 (1929).

[5] See Smyth and Stoops, *ibid.*. 51,3312 (1929).

Preparation of Materials

Benzene was purified as in earlier work.[6]

Ethyl Formate.—Material obtained from the Eastman Kodak Company (b. p. 54–55.5°) was dried with anhydrous sodium sulfate and distilled. The fraction boiling at 54.0–54.5° was redistilled and the fraction at 54.2–54.4° taken for use.

Ethyl Acetate.—Merck's ethyl acetate was shaken twice with concentrated potassium carbonate solution, washed with water, dried with fused potassium carbonate and then with phosphorus pentoxide, and fractionally distilled. The middle fraction was redistilled, b. p. 76.7–76.9°.

Ethyl Propionate.—Material obtained from the Eastman Kodak Company (b. p 98–100°) was dried with phosphorus pentoxide and distilled. The middle fraction (b. p. 99.05–99.15°) was redistilled and the fraction at 99.10–99.15° taken for use.

Dibasic Acid Esters.—With the exception of the diethyl ester of hexadecamethylenedicarboxylic acid, the materials were obtained from the Eastman Kodak Company. They were dried over anhydrous sodium sulfate or fused potassium carbonate and fractionally distilled under reduced pressure, the middle fraction being taken and redistilled.

Hexadecamethylenedicarboxylic ester was prepared from the acid, which was very kindly loaned to us by Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company. A solution of the acid in absolute ethyl alcohol was treated with dry hydrogen chloride and, after two hours of refluxing, the excess alcohol was distilled off. After cooling, the product was poured into ice water, treated with sodium carbonate, filtered, washed and dried, It was then recrystallized four times from absolute alcohol and dried in a vacuum desiccator; m. p. 48.3°.

The refractive indices of all the purified liquids are shown in Table I, their good agreement with the values in the literature giving evidence of purity. The molar refraction of the hexadecamethylenedicarboxylic ester given in Table III is calculated from measurements upon the substance in solution. It is only 0.1 higher than the value calculated as the sum of the atomic refractions.

Experimental Results

The data for the pure substances are given in Table I, in which the temperature coefficient of the refractive index for the D sodium line is calculated as the difference between the values at 20 and 25° divided by 5 and the coefficient of the density as the difference between the values at 25 and 50° divided by 25. The indices at 25° and the densities at 50° are omitted for the sake of brevity. In Table II the first column gives the mole fraction c_2 of the ester in the benzene solution and the succeeding columns give the values at 25 and 50° of the dielectric constants ϵ and the densities d of the solutions and the polarizations P_2 of the esters. P_2 is calculated by means of the usual equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{c_1M_1 + c_2M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2 and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. For dilute solutions the difference $P_{12}-P_1$ is so small that the error in P_2 may be large, sometimes,

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[6] Smyth and Rogers, THIS JOURNAL. 52, 2227 (1930).

causing single values of P_2 to deviate markedly from a uniform variation with c_2. In some cases ten or more solutions have been measured in order to fix as accurately as possible the course of the P_2–c_2 curve, although only enough values are included in Table II to make possible the reproduction of the curve. A number of solutions in heptane also were run as a check on those in benzene, but the few data thus obtained are omitted as they are consistent with the results for the benzene solutions. The extrapolation of the P_2–c_2 curve to infinite dilution, that is, $c_2 = 0$, gives the value of P_∞, from which the electric moment μ is calculated by means of the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$$

in which MR_D is the molar refraction calculated from the data in Table I, and T is the absolute temperature. In Table III the second column gives the carbon chain which holds the $—COOC_2H_5$ group or groups, the third column gives the molar refraction for the D sodium line, and the fourth and

TABLE I

REFRACTIVE INDICES AND DENSITIES OF THE ESTERS

	n^{20}_D	$\Delta n/\Delta t \times 10^5$	d^{25}_4	$\Delta d/\Delta t \times 10^5$
Ethyl formate	1.35987	47	0.9071	130
Ethyl acetate	1.37276	51	.8943	123
Ethyl propionate	1.38414	51	.8842	116
Diethyl maleate	1.44085	54	1.0586	101
Diethyl fumarate	1.44095	54	1.0452	103
Diethyl oxalate	1.41044	45	1.0725	117
Diethyl malonate	1.41411	39	1.0525	107
Diethyl succinate	1.42010	40	1.0349	103
Diethyl glutarate	1.42400	40	1.0170	100
Diethyl adipate	1.42740	40	1.0033	96
Diethyl sebacate	1.43672	38	0.9588	84

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS OF THE ESTERS

	ϵ		d		P_2	
c_2	25°	50°	25°	50°	25°	50°
			Ethyl Formate			
0.0000	2.276	2.229	0.8734	0.8468	(26.68	26.80 = P_1)
.0377	2.460	2.387	.8741	.8472	93.0	87.3
.0546	2.541	2.457	.8744	.8475	91.5	86.0
.1126	2.822	2.708	.8756	.8484	87.3	83.6
.1696	3.112	2.960	.8769	.8494	84.4	81.1
.2083	3.312	3.137	.8779	.8502	82.4	79.6
			Ethyl Acetate			
0.0310	2.410	2.341	0.8739	0.8472	91.2	84.2
.0475	2.477	2.400	.8742	.8475	89.0	83.4
.0614	2.532	2.450	.8744	.8476	87.6	83.0
.1060	2.708	2.602	.8752	.8484	84.4	80.3
.1575	2.912	2.782	.8762	.8492	82.0	78.6

TABLE II (*Continued*)

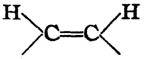
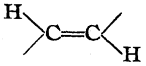
c_2	ϵ		d		P_2	
	25°	50°	25°	50°	25°	50°
Ethyl Propionate						
0.0275	2.388	2.322	0.8736	0.8468	93.2	86.8
.0649	2.534	2.449	.8741	.8471	90.6	85.5
.0900	2.627	2.533	.8744	.8474	88.8	84.8
.1350	2.794	2.684	.8751	.8480	86.7	83.7
Diethyl Maleate						
0.0240	2.481	2.411	0.8813	0.8547	170.5	163.1
.0312	2.542	2.463	.8836	.8571	169.3	161.1
.0574	2.747	2.649	.8919	.8655	162.1	155.9
.0797	2.921	2.807	.8987	.8723	158.3	153.3
.1213	3.216	3.065	.9105	.8841	150.9	146.1
Diethyl Fumarate						
0.0262	2.474	2.405	0.8812	0.8549	157.6	150.9
.0576	2.703	2.611	.8900	.8637	153.3	148.0
.0699	2.793	2.691	.8935	.8672	152.0	146.8
.0878	2.919	2.805	.8984	.8721	149.8	145.1
.1044	3.033	2.907	.9028	.8766	147.8	143.3
Diethyl Oxalate						
0.0318	2.537	2.463	0.8828	0.8561	156.2	150.3
.0492	2.675	2.583	.8879	.8612	152.4	146.0
.0629	2.784	2.680	.8916	.8649	150.2	144.3
.1074	3.104	2.966	.9039	.8771	140.8	136.1
.1381	3.326	3.177	.9121	.8853	136.8	131.2
Diethyl Malonate						
0.0238	2.482	2.412	0.8808	0.8539	167.5	160.8
.0320	2.548	2.470	.8829	.8561	165.1	159.0
.0502	2.706	2.608	.8883	.8615	163.3	156.1
.1087	3.183	3.026	.9045	.8776	153.9	147.9
.1606	3.550	3.362	.9176	.8908	145.1	140.9
Diethyl Succinate						
0.0306	2.457	2.397	0.8829	0.8559	135.3	133.7
.0547	2.596	2.526	.8898	.8630	133.4	132.1
.0729	2.698	2.621	.8949	.8682	132.2	130.8
.0983	2.833	2.748	.9016	.8750	129.8	128.8
.1050	2.871	2.784	.9034	.8768	129.6	128.7
.1531	3.113	3.004	.9153	.8887	126.0	124.8
Diethyl Glutarate						
0.0170	2.405	2.343	0.8782	0.8515	165.5	158.0
.0311	2.510	2.437	.8822	.8555	163.4	157.0
.0544	2.683	2.589	.8886	.8621	161.3	154.7
.0812	2.871	2.762	.8957	.8691	157.7	153.0

TABLE II (*Concluded*)

	ϵ		d		P_2	
	25°	50°	25"	50°	25°	50°
			Diethyl Adipate			
0.0165	2.400	2.339	0.8781	0.8513	169.7	163.8
.0250	2.460	2.392	8805	8537	167.5	161.2
.0367	2.546	2.469	.8838	.8572	167.0	160.9
.0384	2.558	2.480	.8843	.8577	166.6	160.7
.0779	2.832	2.730	.8945	.8683	162 5	158.1
.0836	2 869	2 763	.8960	.8697	161.7	157.4
			Diethyl Sebacate			
0.0119	2.371	2.312	0.8764	0.8496	197.3	189.0
.0182	2.416	2.354	.8779	.8515	193.7	186.7
.0229	2.453	2.383	.8792	.8526	193.9	184.9
.0266	2.480	2.408	.8800	.8536	193.2	185.1
.0273	2.484	2.414	.8802	.8538	192.6	185.8
.0606	2.718	2.619	.8876	.8620	188.7	181.8
			Hexadecamethylenedicarboxylic Ester			
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = P_1)
.00495	2.315	2.260	.8746	.8479	234.8	224.8
.00967	2351	2.291	,8753	.8490	235.6	224.3
.01591	2.395	2.331	.8764	.8504	232.9	224.2
.02736	2.476	2.404	.8784	.8528	232.8	224.9
.03125	2.500	2.427	.8790	.8535	231.2	224.6

TABLE III

ELECTRIC MOMENTS OF ESTERS

	Groups on $-COOC_2H_5$	MR_D	$P_\infty - MR_D$ 25°	50°	$\mu \times 10^{18}$ 25°	50°
Ethyl formate	H—	17.90	78.4	71.5	1.94	1.93
Ethyl acetate	CH_3—	22.28	71.7	63.7	1.86	1.82
Ethyl propionate	C_2H_5—	26.84	68.6	61.1	1.81	1.78
Diethyl maleate		42.68	134.4	125.3	2.54	2.56
Diethyl fumarate		43.26	117.8	110.3	2.38	2.40
Diethyl oxalate	—	33.62	129.4	122.4	2.49	2.52
Diethyl malonate	—CH_2—	37.86	134.7	127.1	2.54	2.57
Diethyl succinate	—$(CH_2)_2$—	42.41	95.4	93.7	2.14	2.21
Diethyl glutarate	—$(CH_2)_3$—	47.01	120.7	112.5	2.41	2.42
Diethyl adipate	—$(CH_2)_4$—	52.08	119.9	112.1	2.40	2.42
Diethyl sebaeate	—$(CH_2)_8$—	70.25	128.7	119.9	2.49	2.50
Hexadecamethylene-dicarboxylic ester	—$(CH_2)_{16}$—	107.0	129.0	117.8	2.49	2.48

fifth columns the differences between this refraction and the values of P_∞ at 25 and 50°. In the calculation of the moment this difference is treated as the orientation polarization, that is, the polarization due to the orientation of the molecular dipoles. This treatment neglects the small atomic polarization P_A, which probably increases somewhat with increase in molecular weight, but, in the case of such large polarizations, the error involved in regarding $P_\infty - MR_D$ as the measure of the effect of the dipole is small.[4] The molar refraction is, of course, the measure of the electronic contribution P_E to the polarization and increases regularly with increase in the size of the molecule. The absolute values of the moments are probably a few hundredths high because of the neglect of P_A, but, relative to one another, they should not be in error by more than $\pm 0.02 \times 10^{-18}$.

Discussion of Results

A few years ago the relative moments of the molecules of monocarboxylic acids and their esters were calculated[7] on the assumption of valences acting at the apices of regular tetrahedra with arbitrarily located charges and complete freedom of rotation about the single bonds. The conclusion reached was that the unsubstituted esters and acids should all have the same moment except for the secondary effects of induction and repulsion between groups. A similar type of calculation for the ketones indicated that they should have moments approximately 1.24 times those of the esters. These conclusions were supported by the values of the moments calculated from the dielectric constants by an approximate method, although, as was to be expected, the replacement of an acid hydrogen by an alkyl group altered the moment considerably. Subsequent work showed that this method of calculating the moment from a single value of the dielectric constant could not be relied upon for accurate results because of its failure to correct wholly for the effect of intermolecular action or association. This was evident to some extent at the time of the calculations on the esters, for ethyl acetate gave a value of 1.47×10^{-18} for the moment at room temperature and 1.62×10^{-18} at the boiling point. This latter value is not much lower than those in Table III for ethyl acetate, which are slightly higher than the unpublished value of Zahn for the vapor, 1.76×10^{-18}, and the value 1.74×10^{-18} found by Williams.[8] It is obvious now, however, that, because of intermolecular action, the small differences in moment calculated in the original investigation were without significance. Recent experimental determinations of the moments of the ketones[9] show that they are about 1.5 times those of the esters, instead of 1.24, as calculated.

Eucken and Meyer[10] have calculated the moments of molecules by assigning definite moments to chemical bonds. Assuming tetrahedral valences and considering the effect of rotation about the C—O bond in fatty

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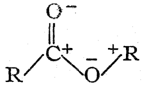
[7] Smyth, THIS JOURNAL, 47, 1894 (1925).

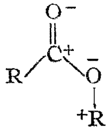
[8] Williams, *Physik. Z.*, 29, 174 (1928).

[9] Wolf and Lederle, *ibid.*, 29, 948 (1928).

[10] Eucken and Meyer, ibid., 30, 397 (1929)

acids and their esters, they have concluded that there are two extreme positions possible, one giving a minimum moment and the other a maximum. These possibilities are evident in the following formulas, in which the principal moments are shown

(a) 

(b) 

For arrangement (a), in which the moments oppose and cancel one another to a considerable extent, Eucken and Meyer calculate a moment 1.1×10^{-18}. (b) is obtained from (a) by a rotation of 180° about the C—O bond. Here the R—O doublet acts in nearly the same direction as the C=O so that the total moment is 3.4×10^{-18}. Intermediate positions about the C—O bond would give intermediate values for the moment. Eucken and Meyer suppose that, in the acids, the tendency of the acid hydrogen to be attracted toward the carbonyl oxygen, the reason for which is evident in the distribution of charges in (a), renders (a) more probable than (b) under ordinary conditions. The moments of the fatty acids should thus be lower than they would be if, in the rotation about the C—O bond, all positions were equally probable. Eucken and Meyer encountered the difficulty that the value found in the literature for the moment of benzoic acid was lower than the minimum value 1.1×10^{-18} calculated for (a). This was also true of values found for several fatty acids.[11] The difficulty appears, however, to be removed by the finding of a value of 1.4×10^{-18} for acetic acid together with evidence that the low values found for other acids were in error because of molecular association.[12]

Although such speculation is necessarily uncertain, it is interesting to note that the tendency of an alkyl group to be attracted toward the carbonyl oxygen might be expected to be less than that of an acid hydrogen. This would make structure (a) represent a less probable position for an ester than for an acid so that the former would have a larger moment as shown by the values for the monocarboxylic acid esters in Table III when compared with the value 1.4×10^{-18} for acetic acid. As the energy of rotation about the C—O bond increases with rising temperature, the forces which render one position more probable than another have decreasing influence and a condition is approached in which all positions around the bond are equally probable. This reduction[13] in the probability of a structure approximating to (a) should result in an increase in moment with temperature, a phenomenon which has been observed by Zahn[12] for the

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[11] Wolf, *Physik. Z.*, **31**, 227 (1930).

[12] Smyth and Rogers, THIS JOURNAL, 52, 1824 (1930); Zahn, *Phys. Rev.* **35**, 1047 (1930).

[13] Meyer, *Z. physik. Chem.*, [B] 8, 27 (1930).

vapor of acetic acid. If the hypothesis just presented is correct, the esters should show a smaller temperature variation than the acids as their distribution about the C—O bond is a more nearly random one than that of the acids. Actually, Zahn, in measurements as yet unpublished, has found no temperature variation of the moment of ethyl acetate in the vapor state, although a variation might be expected in some region of temperature. The reduction of the mean moment because of the fact that all positions around the C—O bond are not equally probable offers a possible explanation of the high value calculated for the ester as compared to that of the ketone on the assumption of the equal probability of all the positions.

Meyer's calculation of the mutual potential energies of the moments in the —COOH group led to values so high that a temperature of 20,000° would have to be reached for fully excited rotation to occur within the group. If this is correct, the temperature variation which is experimentally possible might well be too small to produce a detectable variation in moment. Zahn attributed the change in the moment of acetic acid vapor which he observed between room temperature and 200° to a transition from one state to a higher state of vibration associated with the —OH group. Meyer calculated 3.5×10^{-18} to be the limiting value of the moment approached at the very high temperatures as the energy of rotation overcomes the mutual attraction of the doublets. This value is actually slightly higher than that calculated by Eucken and Meyer for the structure of maximum moment like that represented by (b). Evidently, attempts at exact calculation of the moments and their temperature changes are exceedingly uncertain, but the hypotheses which have been discussed may be used in a qualitative interpretation of experimental results.

The differences between the moments found at 25 and at 50° for the esters in Table III are no greater than the possible experimental errors except in the case of diethyl succinate. It does not appear significant that the three esters of monocarboxylic acids show a decrease in the values found for the moment from 25 to 50°, while the dicarboxylic acid esters generally show an increase. As it has been shown that any change in the moments of the former esters with rising temperature should be an increase and as Zahn has found no change in the moment of ethyl acetate vapor with temperature, the decrease observed in the moments of the fatty acid esters should be accidental, possibly arising from a small error in the calibration of the cell at the higher temperature. The increase in the moments of the other esters is what would be expected from the increased energy of rotation, but the observed change is too small to be significant without further experimental confirmation except in the case of diethyl succinate.

As the marked drop in moment on passing from the formate to the acetate and the slight drop on passing from the acetate to the propionate are analogous to the sharp drop in ionization constant on passing from formic to acetic acid and the smaller drop from acetic to propionic acid, it would appear that there is a slight variation in the polarity of the O—R bond with the nature of the group attached to the carboxyl carbon. Naturally, the change from hydrogen to methyl has a greater effect than that from methyl to ethyl. It may be noted that the moment of ethyl benzoate is 1.8 X 10^{-18},[14] which shows that the phenyl group has no markedly different effect upon the —$COOC_2H_5$. It seems reasonable to assign a value 1.8 × 10^{-18} to the moment of the —$COOC_2H_5$ group when it is attached to a carbon atom, but this moment cannot be treated like that arising from a simple atom or group such as chlorine or nitro because of the effects of the rotation within the group and of the rotation of the group itself. The mean effective moment of the group probably makes an angle with the direction of the bond connecting the group to the rest of the molecule not very different from the tetrahedral angle, but the complexity of the structure arising from rotation and the approximations which would be necessary, render useless an attempt to calculate this angle exactly. If the moment is treated as a fixed moment 1.8 X 10^{-18}, making the tetrahedral angle 110° with the direction of the bond of the group, the moment resulting from the joining of two groups to form diethyl oxalate may be calculated from the simple equation, $\mu = 1.41 \times 1.8 \times 10^{-18} \sin 70° = 2.4 \times 10^{-18}$,[15] in which the effect of the two groups upon each other is disregarded. This value is close to that observed for diethyl oxalate, in which, however, the fields of force of the two groups should so affect one another that some positions in the rotation of the groups about the connecting bond should be much more probable than others. In dimethyl terephthalate, two —$COOCH_3$ groups, which should have moments close to those of the —$COOC_2H_5$, though, perhaps, a little lower, are in para positions on the benzene ring. As the benzene valences lie in the plane of the ring directed out from the center,[16] this means that the two groups are placed relatively to one another just as in the oxalate, except that they are so far separated from one another by the benzene ring that all positions of rotation about the line joining the two carbonyl carbons should be equally probable. The moment found for this molecule,[17] 2.2 X 10^{-18}, differs from the calculated value by little more than the possible experimental error. The moment 2.5 X 10^{-18} found by the same investigators for dimethyl o-phthalate in which the two —$COOCH_3$ are attached to the ring in such a way that the group bonds make an angle of 60° with one another instead of pointing in opposite directions shows that the resultant

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[14] Estermann, *Z. physik. Chem.*, [B] 1, 422 (1928).

[15] *See* Williams, *ibid.*, [A] 138, 75 (1928).

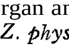
[16] Smyth and Morgan, THIS JOURNAL, 49, 1030 (1927).

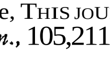
[17] Estermann, Ref. 14; Weissberger and Williams, *ibid.*, [B] 3, 367 (1929).

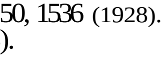
moment of the molecule is increased, but only to a small extent, by the introduction of this angle. This is in marked contrast to the behavior of simple groups, for the moment of *p*-dichlorobenzene is zero, while that of o-dichlorobenzene is 2.25 X 10^{-18}.[18]

In diethyl fumarate the two $—COOC_2H_5$ groups should point in opposite fixed directions and the moment happens to be identical with that calculated for such an arrangement. It must be remembered in considering all of these calculated values that, while, relative to one another, they are significant, absolutely, they can be expected to indicate little more than the order of magnitude. In diethyl maleate the groups make an angle with one another, perhaps acute, and the moment is 0.16×10^{-18} higher than that of the fumarate, the difference resembling qualitatively that between the ortho and para arrangements of similar groups on the benzene ring. That the force fields of the groups affect one another strongly in the cis form is shown by the fact that the first ionization constant of maleic acid is ten times that of fumaric, while the second ionization constant of fumaric is about one hundred times that of maleic. The moment of the maleate is probably influenced by the effects of the two groups upon one another, but, in view of the small differences in moment accompanying great differences in the angles between the groups, the effect of the groups upon one another's rotation about the group bonds should not alter the moment greatly. It is evident also that the moment of the molecule as a whole is little affected by possible effects upon the rotation about bonds within the $—COOC_2H_5$ groups.

The insertion of the $—CH_2—$ between the $—COOC_2H_5$ groups to form the malonate should introduce the tetrahedral angle between them, that is, set them at an angle of 110° to one another and so raise the moment slightly as observed in Table III. When another $—CH_2—$ is introduced to form the succinate, the effect is complicated by rotation about the bond between the $—CH_2—$ groups. However, it is customary to regard a carbon chain as a zig-zag arrangement and Vorländer[19] has found that the tendency to form liquid crystals, which is dependent, to a considerable extent, upon the linearity of the molecules, is greatly reduced by the introduction of a $—CH_2—$ group into the middle of the molecule of a liquid crystalline substance because of the angle thereby produced in the chain of the molecule. When a second $—CH_2—$ group is added, the tendency to form liquid crystals is largely restored, while the addition of a third $—CH_2—$ reduces the tendency once more, etc. The bending of the molecule is obvious if we write the carbon-to-carbon valences in the conventional fashion







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[18] Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928).

[19] Vorländer, *Z. physik. Chem.*, 105,211 (1923).

It would appear that there is a tendency toward such a zig-zag arrangement, but rotation about the bonds in the molecules containing more than one carbon between the $—COOC_2H_5$ groups gives the opportunity for all possible arrangements, of which, perhaps, the zig-zag is the most probable. In considering the moments of the molecules containing the $—COOC_2H_5$ groups on the ends of these chains, one must bear in mind that not only the orientations of the two groups relative to one another, but also the removal of the two groups from one another's influence by the interposition of carbon atoms may affect the resultant moment of the molecule as a whole.

The rise in moment from the oxalate to the malonate is followed by a drop as expected on going to the succinate, but the magnitude of the drop shown in Table III is much greater than would be expected. When the result was first obtained, the presence of an abnormally large experimental error was suspected, but the purity of the material used was checked satisfactorily and additional measurements agreed with the first. It is possible that the apparent farther removal of the $—COOC_2H_5$ groups from one another's influence has some effect, but, if this were the principal cause of the drop, one would expect the moments of the higher members of the series to vary around 2.2×10^{-18} instead of rising again to above 2.4×10^{-18}. Actually, there is reason to believe that, instead of being farther removed from one another, parts, at least, of the $—COOC_2H_5$ groups in the succinate may be particularly close to one another, for the anhydride of succinic acid is formed with ease. Dunstan, Hilditch and Thole[20] found that the molecular viscosities of these esters gave a smooth curve when plotted against molecular weight except for a sharp hump at the value for the succinate, which lay above those for the malonate and the glutarate. This enhancement of the viscosity was attributed to contiguity of the groups at the ends of the carbon chain. It seems probable then that the structure with two carbons between the $—COOC_2H_5$ groups is particularly favorable to those positions of rotation about the bonds in which certain of the doublets are brought close together so as partially to oppose and cancel one another, the mean resultant moment of the molecule being thereby lowered. This idea receives support from the marked rise in moment when the temperature changes from 25 to 50°, for rising temperature, by tending to make all positions equally probable, would increase the moment. It would appear that the succinate is the only one of these esters which may be expected to show much variation of moment with temperature since, in the others, the influences of the $—COOC_2H_5$ groups upon one another have little effect upon the resultant moment of the molecule. It may be mentioned that, in examining the optical activity of the menthyl esters and the brucine salts of the fatty dibasic acids, Hilditch[21] found

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[20] Dunstan, Hilditch and Thole, *J. Chem Soc.*, **103, 133** (1913).

[21] Hilditch, *ibid.*, 95, 1678 (1909).

an exceptionally large temperature coefficient for the rotatory power of dibrucine succinate. The temperature variation of the moments of these substances is being further investigated.

The moment of the glutarate should be approximately the same as that of the malonate if the zig-zag structure of the carbon chain and the consequent angle between the $—COOC_2H_5$ groups were maintained, but rotation about the bonds of the chain tends to destroy this arrangement and lower the mean moment. Because of this rotation and flexibility of the chain, the effect of an added carbon atom diminishes with increasing length of the chain. In fact, the fourth carbon added in going from the glutarate to the adipate has no observed effect. If, therefore, the chain does not bend around upon itself with increasing length to form something like a loose ring structure because of the attraction of the $—COOC_2H_5$ dipoles for one another, and if it is not so flexible as to bend in the electric field used in the measurement of the dielectric constant and so give partially independent orientation of the two ends of the molecule in the field, the value found for the moment should show little change with increasing length of the chain. The small apparent increase in moment from the adipate to the sebacate might be attributed in part to the neglected P_A of the four added $—CH_2—$ groups and in part to the effects just mentioned, but the absence of further change when the chain is lengthened by eight more $—CH_2—$ groups indicates that these effects must be very small. Indeed, if the atomic polarization, P_A, of the eight $—CH_2—$ groups were equal to that of octane,[22] 0.78, it would increase the apparent value of the moment by less than 0.01×10^{-18}. Although it has been shown that the orientation of the $—COOC_2H_5$ groups relative to one another does not have a large effect upon the moment of the molecule, the identity of the moment of the very long molecule of the diethyl ester of hexadecamethylenedicarboxylic acid with that of the shorter molecule of the sebacate and the closeness of this value to those for the relatively short molecules would seem to indicate that the long chains do not bend around upon themselves to form ring structures. It would further appear that the extended chains of the long molecules are not so flexible as to bend in the external fields applied in the measurements.

Summary

The dielectric constants and densities of the ethyl esters of a number of mono- and dicarboxylic acids have been measured in benzene solution and have been used, together with the refractions determined for the pure substances, to calculate the electric moments of the molecules. The ethyl esters of the monobasic fatty acids show a slight decrease in moment with increase in the size of the molecule analogous to the decrease in ionization constant.

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[22] Dornte and Smyth, THIS JOURNAL, 52, 3546 (1930).

Because of rotation around the bonds the relative positions of the $—COOC_2H_5$ groups in the molecule do not have large effects upon the moment.

The absence of marked difference in moment between the long and the short-chain esters is regarded as indicating that the long-chain molecules have extended structures, which do not bend appreciably in small external electric fields.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE RAPID COLORIMETRIC ESTIMATION OF POTASSIUM

BY EARLE R. CALEY

RECEIVED DECEMBER 4, 1930 PUBLISHED FEBRUARY 9, 1931

Some months ago the writer published a paper[1] setting forth the merits and demerits of the picric acid test for potassium from a qualitative point of view. Further experiments have since demonstrated that this reaction may be utilized for the colorimetric estimation of small amounts of potassium by separating the precipitated potassium picrate, dissolving it in water, and using the intensely-colored yellow solution thus obtained for the determination of the element.

Factors Influencing the Quantitative Precipitation of Potassium as Picrate by Alcoholic Solutions of Picric Acid.—In addition to the marked influence of the ratio of the volume of the reagent to that of the potassium solution on the sensitivity of the reaction, noted in the previous paper, it was found that the temperature during precipitation was of importance from the quantitative standpoint. In the accompanying graph are shown the results of several experiments (Fig. 1) in which the amount of potassium picrate precipitated at various room temperatures is compared colorimetrically with that precipitated at 20°. This effect is apparently due to the rapid increase in the solubility of the precipitate with rise in temperature. It is evident that for comparative quantitative results in any colorimetric method involving this reaction the potassium, in a single series of experiments where standards and samples are prepared for matching, they must be precipitated under like temperature conditions or, better, a definite temperature must be established for all precipitations. It is apparent from the graph that for the sake of greater completeness of precipitation this temperature should be nearer the lower limits of room temperature rather than the higher. A temperature of 20° was found to be satisfactory. Temperatures much below this, while resulting in the more complete precipitation of the potassium, are not satisfactory due to the precipitation of the picric acid from the reagent saturated at room temperature and to

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[1] Caley, THIS JOURNAL, 52, 953 (1930).

increased interference from sodium. The influence of agitation and time of standing on completeness of precipitation were also studied. It was found that a forty-five-minute period of standing with occasional stirring was adequate in all cases providing the solution was stirred sufficiently at the beginning to start the separation of the precipitate when dealing with amounts of potassium near the lower limit of precipitation.

Experiments on Methods of Collecting and Washing the Precipitated Potassium Picrate.—The nature of the reagent introduced certain difficulties in the way of sharply separating the precipitate from the excess of reagent. Due to the direct dyeing action of picric acid, filtering mediums containing minute pores, such as filter paper and even asbestos, were found to be unsuitable. A number of experiments demonstrated that it was extremely difficult completely to wash out the picric acid from such filters, with any liquids suitable for this purpose, without applying an excessive number of washings, and yet on the subsequent dissolution of the precipitate in water variable amounts of the remaining picric acid went into solution, thus introducing sensible errors in the colorimetric comparison. It was found, however, that the use of a medium-porosity, sintered-glass filtering funnel or crucible permitted the sharp separation of the precipitate and excess reagent with ease. The picric acid is apparently not adsorbed in such glass filters and is readily removed with a few washings. Several washing mediums were tried, such as 95% alcohol, 95% alcohol saturated with potassium picrate and ethyl ether. It was found that the latter was the most satisfactory of these due to the ready solubility of picric acid and the high insolubility of potassium picrate in this liquid.

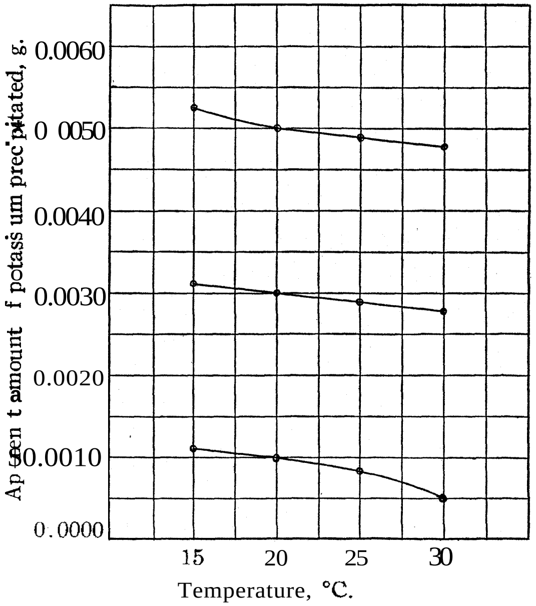

Fig. 1.—Showing the effect of temperature on completeness of precipitation in the reaction between potassium chloride solutions and saturated alcoholic solutions of picric acid.

Accuracy Obtainable in the Colorimetric Comparison of Potassium Picrate Solutions.—In order to ascertain the observational error inherent in matching solutions of potassium picrate, experiments were performed in which the same solution was divided and comparison made between the two parts in a plunger type colorimeter. The following table gives the results obtained with solutions of different concentration and shows the average values of the pairs of colorimeter readings after two, five and ten successive observations.

TABLE I

OBSERVATIONAL ERRORS IN THE COMPARISON OF IDENTICAL POTASSIUM PICRATE SOLUTIONS

Concn. of potassium, g./cc.	Averages of readings after two comparisons, mm.	Errors, %	Averages of readings after five comparisons, mm.	Errors, %	Averages of readings after ten comparisons, mm.	Errors, %
0.00002	L 29.0		L 28.2		L 28.9	
	R 28.2	2.8	R 27.9	1.1	R 28.6	1.0
.00010	L 10.7		L 12.1		L 11.1	
	R 10.6	0.9	R 12.0	0.8	R 11.1	0.0
.00020	L 11.1		L 9.9		L 9.4	
	R 10.4	6.3	R 9.7	2.0	R 9.5	1.1

From the above results it is evident that solutions of the concentrations shown may be balanced colorimetrically with an error of not more than about 1% providing at least ten separate observations are made and the results of these averaged. Solutions of potassium picrate much outside the range of concentration shown in the above table cannot be matched with this degree of accuracy. For amounts of potassium from one to ten milligrams the above experiments also indicated that a solution of the corresponding amounts of potassium picrate in fifty cubic centimeters of water would yield solutions of proper concentration for accurate matching. The best conditions for matching such solutions appear to be reached when depths of solution are used that show a strong straw color and when a strong white light is used as the source of illumination.

Recommended Procedure.—On the basis of the experiments outlined above the following method was evolved.

Procedure

Evaporate the solution, containing the potassium *as* the chloride, to dryness on the steam-bath in a 25-cc. beaker. Dissolve the residue in 1.00 cc. of water and add, with stirring, 7.5 cc. of a saturated solution of pure picric acid in 95% alcohol. Place the beaker in a dish containing water at 20° to maintain a definite temperature during precipitation and, if necessary, stir the solution until a precipitate starts to form. Let the mixture stand for forty to forty-five minutes and stir at five-minute intervals in order to promote complete precipitation. Filter off the separated potassium picrate in a medium-porosity, sintered-glass filtering funnel or crucible and, after the excess reagent has passed through the filter, transfer the small portion of precipitate remaining in the beaker to the filter by washing out with small portions of ether. Wash the precipitate with successive 1–2 cc. portions of ether until the washings are colorless and no trace of yellow color due to picric acid can be seen in the sintered glass disk or on any part of the filtering crucible or funnel. Usually five to ten washings will be required. Free the precipitate from ether by continuing the suction for about one-half minute after completing the washing and then dissolve the precipitate in successive small portions of water, catching the resulting solution in a 50-cc. volumetric flask. After mixing, compare the yellow solution with a standard potassium picrate solution representing approximately the same amount of potassium. The standards are prepared from a potassium chloride solution of known value by means of the above procedure. A convenient solution for this purpose is one containing 1.907 g. of pure potassium chloride per liter, 1.0 cc. of which represents 0.0010 g. of potassium.

Results Obtained with Known Amounts of Pure Potassium Chloride.—The comparison of samples and standards prepared by the above procedure was found to give satisfactory results in all cases when the amount of potassium present, in the sample and standard compared, was identical or nearly so, as the results in Table II show, while on comparing samples with standards containing different amounts of potassium the results were

TABLE II

THE DETERMINATION OF POTASSIUM IN VARIOUS SAMPLES USING STANDARDS REPRESENTING THE SAME AMOUNTS OF POTASSIUM

Potassium present in		Colorimeter readings (each value the mean of ten observations)		Potassium found, g.	Differences, g.
Standards, g.	Samples, g.	Standards, mm.	Samples, mm.		
0.0010	0.0010	27.9	29.6	0.0009	−0.0001
	.0010	29.7	31.0	.0010	.0000
	.0010	27.0	25.5	.0011	+ .0001
	.0010	29.8	27.6	.0011	+ .0001
	.0010	31.7	31.4	.0010	.0000
.0015	.0015	26.0	25.6	.0015	.0000
	.0015	26.2	25.8	.0015	.0000
.0020	.0020	17.9	17.7	.0020	.0000
	.0020	20.1	19.8	.0020	.0000
.0030	.0030	27.3	27.2	.0030	.0000
	.0030	25.0	24.6	.0030	.0000
.0050	.0050	17.5	17.3	.0051	+ .0001
	.0050	17.9	17.8	.0050	.0000
.0100	.0100	10.2	10.0	.0102	+ .0002
	.0100	10.8	10.5	.0103	+ .0003
	.0100	10.4	10.3	.0101	+ .0001

not satisfactory in those cases where the amount of potassium present in the sample was less than three milligrams, as indicated in Table III.

TABLE III

THE DETERMINATION OF POTASSIUM IN VARIOUS SAMPLES USING STANDARDS REPRESENTING DIFFERING AMOUNTS OF POTASSIUM

Potassium present in Standards, g.	Potassium present in Samples, g.	Colorimeter readings (each value the mean of ten observations) Standards, mm	Colorimeter readings (each value the mean of ten observations) Samples, mm	Potassium found, g.	Differences, g.
0.0015	0.0010	15.5	34.9	0.0007	−0.0003
	.0010	14.3	28.9	.0007	− .0003
	.0010	16.0	34.5	.0007	− .0003
	.0010	14.6	32.2	.0007	− .0003
.0020	.0010	9.2	30.2	.0006	− .0004
	.0010	8.5	28.9	.0006	− .0004
.0020	.0015	22.8	32.4	.0014	− .0001
	.0015	20.6	30.1	.0014	− .0001
	.0015	18.6	26.4	.0014	− .0001
	.0015	21.5	31.9	.0013	− .0002
.0030	.0015	13.3	31.0	.0013	− .0002
	.0015	14.0	34.3	.0012	− .0003
.0030	.0020	18.6	32.5	.0017	− .0003
	.0020	16.7	29.7	.0017	− .0003
.0050	.0020	11.0	33.6	.0016	− .0004
	.0020	11.7	36.2	.0016	− .0004
.0050	.0030	14.5	25.2	.0029	− .0001
	.0030	14.9	25.4	.0029	− .0001
	.0030	15.8	25.9	.0031	+ .0001
.0100	.0050	12.2	24.0	.0051	+ .0001
	.0050	12.1	24.3	.0050	.0000

This divergence can be attributed to the fact that, due to solubility, a certain constant amount of potassium picrate remains unprecipitated, an effect that yields disproportionate variations in comparing samples containing the lower amounts of potassium with standards containing considerably higher amounts and *vice versa.* This source of error can be obviated entirely by making comparisons only between samples and standards containing approximately the same amounts of potassium as recommended in the procedure. In practice it was found that the use of a series of standards containing 0.0010, 0.0012, 0.0015, 0.0020, 0.0025, 0.0030, 0.0050 and 0.0100 g. eliminates this source of error and gives results on all amounts of potassium within this range as satisfactory as those shown in Table II, especially if care is taken to compare a given sample with the higher standard in cases where the sample is found to lie between two standards in the above series. Such a series of standards appears to be quite permanent, even over a period of a year, if care is taken to guard against loss by evaporation. This method is not suitable for the determination of amounts of potassium much greater than 0.0100 g., due to the increased difficulty in matching such intensely-colored solutions, nor is it suitable for amounts below 0.0010 g. by reason of the fact that precipitation of amounts below 0.0006 to 0.0007 g. does not occur with the volumes of test solution and reagent given in the procedure. By reducing these latter volumes in proportion, amounts below 0.0010 g. can be estimated but this modification is not advisable due to increased manipulative difficulties and to increased interference from sodium.

Effect of the Presence of Other Substances.—As pointed out in the previous paper[1] the potassium and other metals can be present only as chlorides by reason of the nature of the reagent. Sulfates can be transposed in the usual way by means of barium chloride. Small amounts of insoluble substances such as dehydrated silica and barium sulfate do not interfere. The influence of sodium and other metals likely to be associated with potassium is shown in Table IV. Experiments with ammonium, rubidium and cesium are not included in the table since these behave in practically the same manner as potassium. Such interference is not im-

TABLE IV

INFLUENCE OF THE PRESENCE OR SMALL AMOUNTS OR OTHER METALLIC CHLORIDES ON THIS METHOD FOR TKE COLORIMETRIC ESTIMATION OF POTASSIUM

Element present	Amount of element present, g.	Potassium Present, g.	Potassium Found, g.	Differences, g.
Na	0.005	0.0010	0.0010	0.0000
	.006	.0010	.0009	− .0001
	.007	.0010	.0009	− .0001
	.008	.0010	.0038	+ .0028
	.009	.0010	.0052	+ .0042
Na	.005	.0050	.0048	− .0002
	.006	.0050	.0051	+ .0001
	.007	.0050	.0051	+ .0001
	.008	.0050	.0067	+ .0017
	.009	.0050	,0094	+ .0044
Li	.010	.0010	.0009	− .0001
	.010	.0050	.0050	.0000
Na	.005	.0050	.0050	.0000
Li	.005			
Mg	.005			
Ca	.005			
Ba	.005			
Sr	.005			
Li	.010	.0050	.0050	.0000
Mg	.010			
Ca	.010			
Al	.010			
Fe^{+++}	.010			

portant, however, since ammonium is readily removed and rubidium and cesium are so rarely met with in weighable quantities. The interference from sodium is more serious and restricts the method to the examination of samples or residues weighing not more than twenty milligrams in cases where the sodium content is entirely unknown. Where the sodium content is approximately known, larger samples may, in many cases, be used. The other common metals usually associated with potassium apparently do not interfere even when present in larger amounts than shown in the typical experiments recorded in the table. This method is more particularly suitable for the rapid estimation of potassium in small residues of alkali and alkaline earth salts and is convenient where a series of determinations is to be made.

Summary

There has been described a rapid method for the colorimetric estimation of potassium depending upon its precipitation as potassium picrate by an alcoholic solution of picric acid with the subsequent solution of the separated precipitate in water, yielding a highly-colored solution suitable for colorimetric comparison with standard solutions prepared in a like manner from known amounts of potassium.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. II. TERTIARY BUTYL AND TRIPHENYLMETHYL CHLORIDES AND ALCOHOLS

BY C. P. SMYTH AND R. W. DORNTE

RECEIVED DECEMBER 6, 1930 PUBLISHED FEBRUARY 9, 1931

In an earlier paper[1] it has been shown that the relation between electric moment and chemical behavior is usually slight, but it has seemed desirable to pursue the investigation further for the case of a few closely related groups of markedly different chemical behavior. For this purpose, the n-butyl, *tert.*-butyl, and triphenylmethyl groups seemed particularly suitable. The n-butyl alcohol[2] and chloride[3] having already been investigated, the corresponding *tert.*-butyl and triphenylmethyl compounds were measured. While the determinations were being made, Parts[4] published values for the moments of the primary, secondary and tertiary butyl halides, which will be used in the subsequent discussion. It was hoped that the polariza-

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[1] Smyth, THIS JOURNAL, 51,2380 (1929).

[2] Miles, *Phys. Rev.*, 34, 964 (1929); Smyth and Stoops, THIS JOURNAL, 51, 3312 (1929).

[3] Smyth and Rogers, *ibid.*, 52, 2227 (1930).

[4] Parts, *Z. physik. Chem.*, [B] 7,327 (1930).

tion–concentration curves obtained in the measurements would give qualitative information concerning the effects of the shapes of the groups upon the action of the molecular fields of force.

Preparation of Materials

Heptane and benzene were obtained as in previous work.[3]

***Tert.*-butyl** Chloride.—The material was prepared by Mr. George Rigby working with Professor James F. Norris at the Massachusetts Institute of Technology. It was made from a good grade of *tert.*-butyl alcohol by the action of concentrated hydrochloric acid, washed with a dilute solution of sodium bicarbonate and then with water, distilled and fractionated twice. The part boiling at 50.7° was shaken with anhydrous potassium carbonate for six hours and fractionated twice. After standing for twelve hours with phosphorus pentoxide, it was distilled, treated again with phosphorus pentoxide and redistilled; b. p. 50.7° with a maximum range of 0.05"; n^{20}_{D} 1.38528.

***Tert.*-butyl** Alcohol.—Material given us by Dr. H. B. Glass of Johns Hopkins University was redistilled, as it had stood for some time; b. p. 82.6–82.8°; n^{20}_{D} 1.38777.

Triphenylchloromethane.—Material obtained from the Eastman Kodak Company was twice recrystallized from carefully dried benzene and washed thoroughly with ether; m. p. 111".

Triphenylcarbinol.—Material prepared by Dr. R. H. Smith working with Professor Donald H. Andrews of Johns Hopkins University was loaned to us; m. p. 162°.

Method of Determination

The dielectric constants, ϵ, and densities, d, were measured with the apparatus used in previous work,[5] the former being determined at a wave length of 600 meters. The determinations were made at fixed temperatures with 10° intervals in the case of the *tert.*-butyl chloride and 20° intervals for the other substances. The polarizations, P_2, of the polar components of the solutions were calculated by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{c_1M_1 + c_2M_2}{d} \quad \text{and} \quad P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2 and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. The values of P_2 have been plotted against those of c_2 (see Fig. 1 and Fig. 2) and extrapolated to $c_2 = 0$ to obtain the values of P designated as P_∞. The values of P_∞ when plotted against $1/T$ should give a straight line, as required by the Debye equation, $P = a + b/T$, in which $a = P_E + P_A$, the sum of the electronic polarization, P_E, and the atomic, P_A, and $b = 4\pi N\mu^2/9k$, N being the Avogadro number, 6.061×10^{23}, μ, the electric moment, and k, the molecular gas constant, 1.372×10^{-16}. In the case of *tert.*-butyl chloride, the intercept and slope of this straight line give values of a and b, from which the moment is calculated. However, the solutions of *tert.*-butyl alcohol in heptane, like those of the normal alcohol previously investigated,[2] are so strongly affected by association that the values obtained for P_∞ are not those for

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[5] Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928); Smyth and Morgan, *ibid.*, 50, 1547 (1928); Dornte and Smyth, *ibid.*, 52, 3546 (1930).

molecules oriented at random and actually increase sharply with rising temperature instead of decreasing. As these values could not be used to determine the moment, the alcohol was also run in benzene solution, in which the effect of association was reduced. Because of their low solubility in heptane, the triphenylmethyl compounds also were measured in benzene solution. Unfortunately, the shorter temperature range within which benzene is liquid renders the location of the $P_\infty - 1/T$ curves inaccurate for these solutions. It has seemed best, therefore, to disregard P_A for these substances and use for P_E the molar refraction for the sodium D line, MR_D, which is slightly higher than P_E, a fact which partially compensates for the neglect of P_A. In the alcohol values, at any rate, the error caused by the effect of molecular association is greater than the small error due to neglect of P_A. Instead of using the constant $(P_\infty - a)T = b$ for the calculation of the moment as in the case of *tert.*-butyl chloride, we obtain an approximately constant value for the quantity $(P_\infty - MR_D)T$, calculate the moment from the value at each temperature by means of the relation $\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$, which follows from the preceding equation, and take the mean of the values obtained.

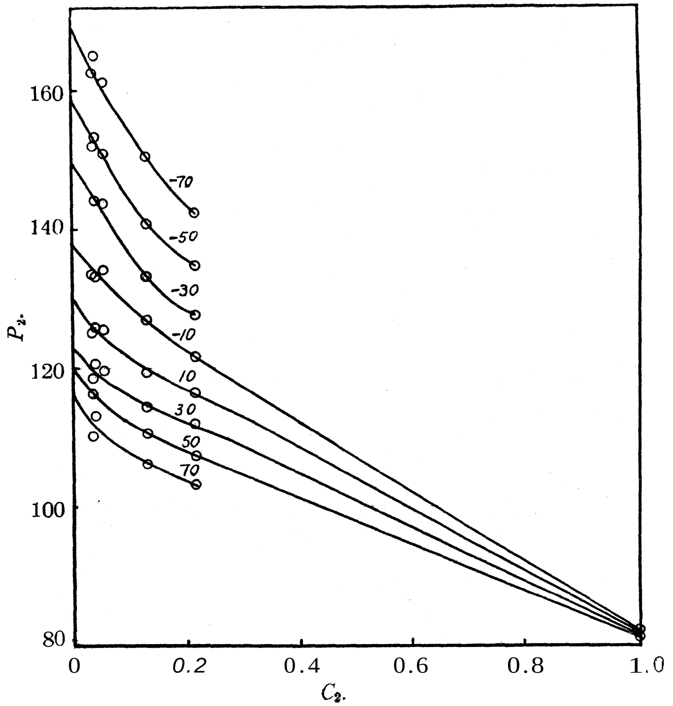

Fig. 1.—Polarizations (P_2) of *tert.*-butyl chloride in solution in heptane.

The experimental results and the values calculated from them are shown in Tables I and II. For the sake of brevity, half of the values obtained for *tert.*-butyl chloride are omitted, the data being given at 20° intervals only.

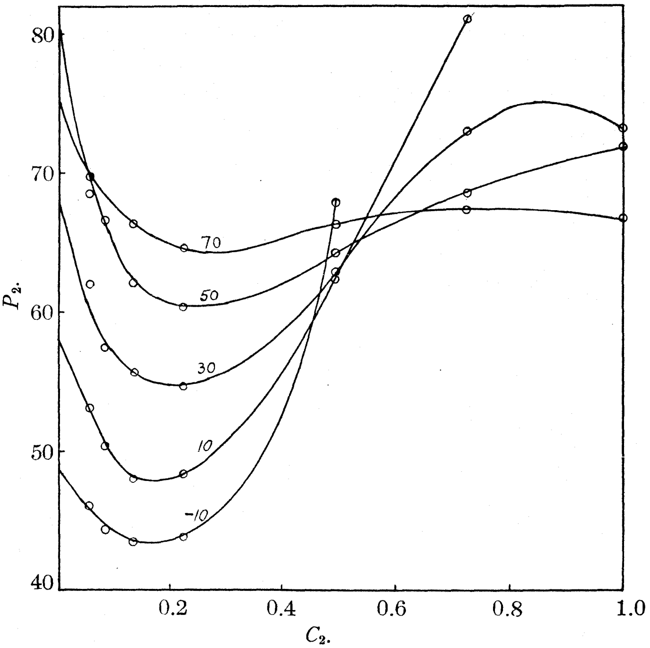

Fig. 2.—Polarizations (P_2) of *tert.*-butyl alcohol in solution in heptane.

Table III gives what appear to be the best values of the moments. The values for MR_D given in Table II are calculated from our measurements of the refractive indices of the pure liquids or of the substances in solution. The value of P_E for *tert.*-butyl chloride was obtained by extrapolation to infinite wave length.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATIONS OF POLAR COMPONENTS

Heptane–*Tert.*-butyl Chloride

Mole fr. of $(CH_3)_3CCl$ = t, °C.	0	**0.0389**	**0.0543**	**0.1309**	0.2156	*1 000*
			ε			
−70	2.048	2.289	2.381	2.892	3.559	
−50	2.020	2.231	2.314	2.754	3.335	
−30	1.992	2.179	2.258	2.641	3.141	
−10	1.966	2.129	2.199	2.546	2.981	11.72
10	1.939	2.084	2.144	2.447	2.849	10.34
30	1.910	2.042	2.095	2.366	2.720	9.23
50	1.879	2.000	2.053	2.292	2.598	
70	1.848	1.960	2.007	2.219	2.487	

TABLE I (*Continued*)

Mole fr. of $(CH_3)_3CCl$ = t, °C.	0	0.0389	0.0543	0.1309	0.2156	1.000
−70	0.7585	0.7632	0.7652	0.7759	0.7886	
−50	.7421	.7470	.7485	.7592	.7713	
−30	.7259	.7305	.7322	.7423	.7539	
−10	.7095	.7140	.7155	.7250	.7363	0.8796
10	.6926	.6968	.6984	.7076	.7183	.8556
30	.6756	.6798	.6814	.6897	.7002	.8316
50	.6581	.6621	.6636	.6715	.6816	
70	.6398	.6430	.6453	.6527	.6620	
	P_∞	$P_2((CH_3)_3CCl)$				
−70	168.9	165.5	161.3	150.5	142.3	
−50	159.0	153.4	151.0	140.7	134.7	
−30	149.2	144.3	144.1	133.2	127.6	
−10	137.8	133.3	134.3	127.0	121.7	82.19
10	130.1	126.0	125.7	119.4	117.1	81.85
30	123.3	121.6	120.0	114.5	112.2	81.54
50	120.9	117.3	118.1	110.6	107.5	
70	117.3	113.9	114.5	106.2	103.2	

Heptane–*Tert.*-butyl Alcohol

Mole fr. of $(CH_3)_3COH$ = t, °C.	0.0585	0.0853	0.1344	0.2259	0.4957	0.7265	1.000
	ϵ						
−50	2.056	2.067					
−30	2.037	2.058	2.084	2.167			
−10	2.018	2.037	2.076	2.168	3.316		
0					3.117	7.33	
10	2.004	2.027	2.069	2.178	3.026	6.21	
30	1.991	2.016	2.072	2.197	2.958	4.91	10.92
50	1.972	2.007	2.066	2.204	2.920	4.28	8.49
70	1.934	1.981	2.045	2.193	2.889	3.99	6.89
	d						
−50	0.7456	0.7470					
−30	.7293	.7305	0.7336	0.7401			
−10	.7125	.7139	.7169	.7234	0.7455		
0					.7370	0.7635	
10	.6954	.6969	.6997	.7062	.7279	.7541	
30	.6781	.6794	.6820	.6882	.7096	.7348	0.7775
50	.6599	.6611	.6635	.6694	.6903	.7146	.7563
70	.6417	.6422	.6441	.6494	.6694	.6932	.7343
	P						
−50	37.7	36.1					
−30	42.1	42.1	39.4	40.4			
−10	46.2	44.3	43.5	43.8	67.9		
10	53.1	50.4	48.0	48.4	62.4	81.0	
30	62.0	57.5	55.4	54.7	62.9	73.0	73.2
50	69.7	66.6	62.1	60.4	64.3	68.6	69.9
70	68.5	70.5	66.3	64.6	66.3	67.4	66.8

TABLE I (*Concluded*)

Benzene–*Tert.*-butyl Alcohol

Mole fr. of $(CH_3)_3COH$ = t, °C.	0	0 0133	0 0264	0 0477	0 1159
10	2.301	2.355	2.403	2 439	2.681
30	2.263	2.314	2.356	2.392	2.646
50	2 17	2.259	2.297	2.341	2.588
70	2.176	2.208	2.239	2.280	2.514
			d		
10	0.8891	0.8876	0.8857	0.8796	0.8752
30	.8676	.8658	.8640	.8579	.8532
50	.8460	.8439	.8421	.8360	.8313
70	.8239	.8219	.8201	.8145	.8083
	P_∞		$P_2((CH_3)_3COH)$		
10	90.0	84.4	82.6	71.0	72.0
30	92.4	88.2	82.3	71.5	74.9
50	80.4	75.5	74.7	70.7	75.3
70	69.5	65.8	66.9	65.1	73.8

Benzene–Triphenylchloromethane

Mole fr. of $(C_6H_5)_3CCl$ = t, °C.		0.0122	0.0282	0.0605	0.0969
10		2.385	2.488	2.692	2.902
30		2.338	2.430	2.622	2.811
50		2.289	2.378	2.553	2.728
70		2.238	2.323	2.481	2.648
			d		
10		0.8990	0.9113	0.9342	0.9575
30		.8777	.8903	.9135	.9372
50		.8561	.8691	.8929	.9170
70		.8343	.8475	.8719	.8966
	Pa,		$P_2((C_6H_5)_3CCl)$		
10	167.3	166.4	164.4	162.9	160.1
30	163.5	163.2	159.0	159.2	155.9
50	157.3	156.7	155.9	155.2	152.4
70	152.3	(146.9)	151.3	150.1	148.7

Benzene–Triphenylcarbinol

Mole fr. of $(C_6H_5)_3COH$ = t, °C.		0.0103	0.0214	0.0375
10		2.352	2.401	2.473
30		2.307	2.356	2.421
50		2.259	2.306	2.368
70		2.208	2.254	2.310
			d	
10		0.8962	0.9037	0.9141
30		.8749	.8825	.8933
50		.8534	.8615	.8722
70		.8310	.8395	.8508
	P_∞		$P_2((C_6H_5)_3COH)$	
10	139.6	137.3	134.6	133.5
30	136.0	133.1	134.2	131.1
50	132.8	125.5	129.6	128.3
70	127.4	(117)	123.6	122.7

TABLE II

VALUES OF $(P_\infty - a)T$, $(P_\infty - MR_D)T$ AND THE MOMENT

$(CH_3)_3CCl$

T, °A.	$(P_\infty - a)T$	T, °A.	$(P_\infty - a)T$
203	27850	283	27850
223	28400	303	27750
243	28500	323	28800
263	27900	343	29300

$a = 31.7$

$b = 28200$

$\mu = 2.14 \times 10^{-18}$

$P_E = 25.3$

$P_A = a - P_E = 6.4$

	$(CH_3)_3COH(MR_D = 22)$		$(C_6H_5)_3CCl(MR_D = 84.0)$		$(C_6H_5)_3COH(MR_D = 80.9)$	
	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
283	19860	1.79	23570	1.95	16670	2.12
303	21280	1.86	24090	1.97	16760	2.13
323	18800	1.74	23680	1.95	16830	2.14
343	16210	1.62	23430	1.94	16020	2.04

TABLE III

MOMENTS X 10^{18}

n-C_4H_9Cl	1 90	n-C_4H_9OH	1 65
$(CH_3)_3CCl$	2 14	$(CH_3)_3COH$	1.65
$(C_6H_5)_3CCl$	1 95	$(C_6H_5)_3COH$	2.11

Discussion of Results

The variation of P_2 for *tert.*-butyl chloride with temperature and concentration is very similar to that of the normal chloride. A 70° rise in temperature lowers the polarization of the pure liquid by only 1.2 in the case of both substances. The values of P_2 for the tertiary chloride are somewhat higher than those for the normal because of the higher moment and the P_2–c_2 curves (Fig. 1) are similar in shape to those for the normal,[3] but slightly steeper, the difference being that which the slightly higher moment should cause. In the study of the alkyl halides just referred to, it was found that there was a slight decrease in the slope of the P_2–c_2 curves in going from ethyl to n-butyl to n-heptyl bromide, although the moments of the three substances were the same This decrease was presumably due to the decrease in the effects of the molecular dipoles upon one another because of the increased screening effects of the larger alkyl groups. It had been thought that the branching of the carbon chain might give increased screening effect, but there is no evidence of such increase in the P_2–c_2 curves for *tert.*-butyl chloride.

The behavior of the alcohols resembles that of the chlorides in that the P_2–c_2 curves for the *tert.*-butyl compound in heptane (Fig. 2) are like those for the *n*-butyl,[2] showing the same peculiar maximum, which flattens with rising temperature, but a more pronounced minimum, also flattening with rising temperature. Intermolecular action is so strong that the apparent values obtained for P_∞ below 50°, not given in Table II, increase with rising temperature instead of decreasing as required by the Debye equation. At 50 and 70° the values of P_∞ agree satisfactorily with those obtained from the benzene solutions, which, as in the case of the benzene solutions of the normal alcohol, conform approximately to the Debye equation. The polarization of the tertiary alcohol at 20°, 75.4, is close to that of the normal compound, 77.3, at the same temperature, but the decrease for the tertiary compound with rising temperature is greater. The small differences in behavior must be due to the difference in the shapes of the carbon chains in the two molecules as the moments are the same. The general similarity in behavior is in accord with the conclusion of Stewart from the x-ray diffractions[6] that when the hydroxyl group is on the first or second carbon of the chain, the molecular arrangement is the same in different alcohols and different from what it is if the hydroxyl group is

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[6] Stewart and Skinner, *Phys. Rev.*, 31, 1 (1928); Stewart, *Chem. Rev.*, 6, 483 (1929); Stewart, *Phys. Rev.*, 35, 726 (1930).

elsewhere. This is borne out by the measurements of Smyth and Stoops,[7] which showed that ethyl, n-butyl, and n-octyl alcohols were similar in behavior while 2-methylheptanol-3 gave P_2–c_2 curves very different in form. The mere assumption that the molecules lie end to end with the OH groups paired when the OH is on the first or second carbon and side by side when it is otherwise located is sufficient to explain the x-ray diffractions but insufficient to explain the dielectric behavior. The complex and unsatisfactory situation in regard to the latter has been discussed in other papers.[8]

The limited solubility of the triphenylmethyl compounds has made it impossible to run P_2–c_2 curves over a sufficient range to warrant their reproduction. However, the values in Table I show that the rates of change of the polarizations of triphenylchloromethane and triphenylcarbinol with concentration are lower than those of the *tert.*-butyl and *n*-butyl compounds, the intermolecular action being less. In other words, the screening effect of the large phenyl groups reduces the action of the molecular dipoles upon one another.

In Table III, 1.90×10^{-18} is given for the moment of n-butyl chloride as the weighted mean of the value 1.88×10^{-18} determined by Smyth and Rogers[3] and 1.97×10^{-18} obtained by Parts,[4] greater weight being attached to the former value because it was. obtained from measurements over a wide range of temperature in which P_A was determined. The value for *tert.*-butyl chloride, 2.14×10^{-18}, is in excellent agreement with the value 2.15×10^{-18} found by Parts. The value 1.65×10^{-18} assigned to n-butyl alcohol is the result of the accurate measurements of Miles upon the vapor [2] It is lower than the value 1.74×10^{-18} obtained from the measurements in benzene previously referred to, which is almost identical with the mean of the values given for the tertiary alcohol in Table II. Because of the agreement of this mean value, 1.75×10^{-18}, with the apparently too high value found for the normal alcohol in solution, and because of the tendency of the values to decrease with increasing temperature, which suggests the possible presence of a small error due to association at the lower temperatures, the value 1.65 is assigned to *tert.*-butyl alcohol. The values for the triphenylmethyl compounds are the means of the values at the different temperatures in Table II, which are in satisfactory agreement with one another.

The difference between the moments of n-butyl chloride and *tert.*-butyl chloride is interesting in view of the theory of induced moments which has been applied[1,3,8] to the alkyl halides. It was shown that the principal doublet in the molecule of a normal alkyl halide exerted an inductive effect upon the carbon chain sufficient to cause a small but appreciable moment in the second carbon of the chain, the moment of the ethyl halide being,

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[7] Smyth and Stoops, THIS JOURNAL, 51, **3330** (1929).

[8] Smyth and Stoops, Refs. 2 and 7; Smyth, ***Chem. Rev.*, 6,** 549 (1929).

as a result, higher than that of the methyl. As lengthening of the chain beyond ethyl did not increase the moment of the molecule, it was concluded that the inductive effect of the principal halide doublet was not sufficient to produce a detectable moment at a distance greater than that of the second carbon atom. In n-butyl chloride, then, only the first and second carbons have sufficient moments induced in them to contribute appreciably to the total moment of the molecule, but, in *tert.*-butyl chloride, there are three carbons approximately at the distance of the second carbon in the normal compound. The small moments induced in each of these three carbons should contribute appreciably to the total moment, which should thus be greater than that of n-butyl chloride. The same should, of course, hold for the bromides and iodides, and this is evident in the values found by Parts, the moments of the tertiary compounds being considerably higher than those of the normal. In the *sec.*-butyl halides, the two carbons next to the first should be affected by the principal doublet so that the total moment should be larger than that of the n-butyl halide and smaller than that of the tertiary. The actual values found by Parts for the *sec.*-butyl halides are between those for the normal and those for the tertiary. In the isobutyl halides the branching of the chain is two carbons away from the principal doublet, so that only two carbons are appreciably affected by the principal doublet just as in the case of the normal compounds. The identical values found by Parts for the n-butyl and the isobutyl compounds are, therefore, to be expected. This view of the effect of induction receives support from the moments found for the heptyl halides by Errera and Sherrill.[9] When the halogen in a heptyl halide is moved from the end of the chain to the second carbon, to which two other carbons are, of course, attached, the moment rises because both of these carbons are now affected by induction. However, moving the halogen farther along the chain to give the 3- or 4-halogenated heptane produces no more effect because the carbons beyond the first two from the halogen in each direction are not affected sufficiently to contribute to the moment.

The absence of an appreciable difference between the moments of n-butyl and *tert.*-butyl alcohols is consistent with the moments of the other alcohols, as there is no significant difference between the values of methyl and ethyl alcohol or of the higher normal alcohols. The moment of the alcohol molecule is the resultant of the moment in the neighborhood of the C–O bond and that in the neighborhood of the H–O bond and this resultant makes a considerable angle with the general direction of the carbon chain,[10] which may account for the absence of inductive effect along the chain. In any event, in the absence of a difference between methyl and ethyl alco-

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[9] Errera and Sherrill, Leipziger Vortrage, 41 (1929); THIS JOURNAL, 52, 1993 (1930).

[10] See Eucken and Meyer, *Physik. Z.*, 30, 397 (1928).

hols, one would not expect the attachment of an increased number of carbons to the first to make much difference in the moment.

The moments found for the triphenylmethyl compounds are difficult to explain. The difference between n-butyl chloride and triphenylchloromethane is too small to be significant. The three benzene carbons attached to the first carbon of the latter compound appear to be less affected by the principal doublet than the three aliphatic carbons in *tert.*-butyl chloride. This is in harmony with the fact that the moment of chlorobenzene, 1.52 × 10^{-18},[5] is lower than those of the higher normal alkyl chlorides. However, this does not account for the high moment of triphenylcarbinol. This might be explained by supposing that the electropositive character of the triphenylmethyl group increases the moment at the C–O bond and thereby increases the total resultant moment. If, however, this is true, why is not the moment at the C–Cl bond increased so as to give triphenylchloromethane a moment higher than that of *tert.*-butyl chloride? The question may be complicated by the existence of the supposed benzenoid and quinonoid structures in the triphenylmethyl compounds, but this tautomerism does not appear to offer any satisfactory explanation of the observed differences.

As before,[1] we thus see very little relation between electric moment and chemical activity. The chemical behavior of n-butyl and *tert.*-butyl compounds, which should depend to a considerable extent upon the nature of the group bond, is markedly different in the two classes of compounds, but the moments of the two alcohols are the same and it is probable that the moments associated with the group bonds in the chlorides are the same, the differences in total moment being due to differences within the groups. The very different triphenylmethyl radical gives no indication of a very different moment associated with the group bond in the chloride, although the high moment of the triphenylcarbinol suggests a difference in the alcohol. The moments of the normal and tertiary butyl compounds can evidently be explained in terms of spatial considerations and induction. It must be remembered that we do not know the cause of the small moment of toluene or of the differences between the moments of the monohalogenated benzenes and the alkyl halides, although they seem quite natural and to be expected. It is not surprising, therefore, that the differences between the triphenylmethyl and the alkyl compounds do not as yet lend themselves to explanation. It may be concluded, however, that the triphenylmethyl compounds show no radical differences in moment corresponding to their different chemical behavior.

Summary

The dielectric constants and densities of solutions of *tert.*-butyl and triphenylmethyl chlorides and alcohols in heptane or benzene have been determined over varying ranges of temperature, and the data have been

used to calculate the polarizations of the substances and the electric moments of their molecules.

The polarizations show that the branched carbon chain of the *tert.*-butyl group has no measurably greater screening effect upon the force field of the dipole than the straight chain of the n-butyl group, while the larger triphenylmethyl group has a greater screening effect.

A theory of induced moments has been applied to explain the values here obtained, together with those of other investigators of alkyl halides. The moments of the molecules increase from the normal to the secondary to the tertiary compound because of the increase in the number of carbon atoms subjected to the inductive influence of the principal dipole, while the moment of the iso compound is the same as that of the normal if the branch in the chain is at least two carbons away from the halogen because only these two carbons are measurably affected by the principal dipole.

As previously observed, the moments do not show differences corresponding to the differences in chemical behavior.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

DIFFERENTIAL POTENTIOMETRIC TITRATION.
IV. (a) AN ADAPTATION OF THE METHOD TO THE USE OF HYDROGEN ELECTRODES.
(b) A TEST OF STANDARDS FOR PRECISE ACIDIMETRY

BY DUNCAN A. MACINNES AND IRVING A. COWPERTHWAITE

RECEIVED DECEMBER 6, 1930 PUBLISHED FEBRUARY 9, 1931

In the third paper of this series[1] an improved apparatus for differential potentiometric titrations, involving a simple gas lift pump, was described, and data were given showing the usefulness of the method for measurements of high precision. We are, however, in this Laboratory, much interested in solutions of acids. Until recently our measurements on conductances, transference numbers, etc., have been hampered by the lack of precise (0.01% or better) methods for acidimetry. This has been especially true with regard to solutions of weak acids. Our attempts to use the quinhydrone electrode for acidimetry were not successful. This was probably due to the rapid oxidation of this substance as soon as the solutions approach the neutral point. An effort was also made to get the desired accuracy by means of indicators, using color standards, without greater success. Either of these methods might, with further investigation, have been developed to give adequate precision. It was, however,

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[1] The papers already published in this series are (a) MacInnes and Jones, THIS JOURNAL, 48, 2831 (1926); (b) MacInnes, *Z. physik.* Chem. (Cohen Festband), 217 (1927); (c) MacInnes and Dole, THIS JOURNAL, 51, 1119 (1929).

decided to adapt the differential potentiometric method to the use of hydrogen electrodes. With such electrodes the results are more nearly unambiguous than when some indicating substance is added, since no allowance need be made for such an addition.

The Apparatus

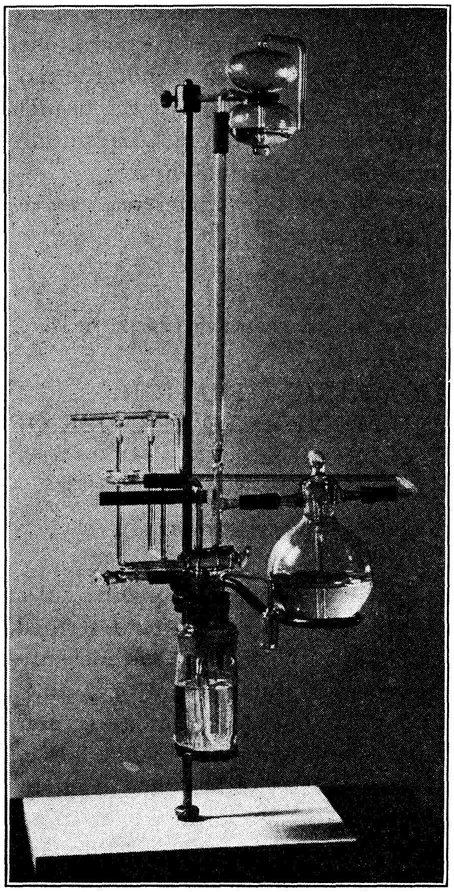

Fig. 1.

The apparatus now in use utilizes the gas lift pump described in a previous paper,[1] operated by a stream of hydrogen. It was found in our early tests that for correct results when using hydrogen electrodes two conditions are essential. First, the apparatus must exclude oxygen during the titration, and, second, no dissolved oxygen should be added with the titrating fluid. The apparatus as finally developed is shown in Fig. 1 and a diagrammatic sketch of the principal parts in Fig. 2. The solution to be titrated is placed in the vessel represented by A, of the latter figure. This is of about 150 cc. capacity. It is closed by a ground-glass joint a-a, into which fits a glass cover containing three openings shaped to hold rubber stoppers. These three openings are at the angles of a triangle in the actual apparatus instead of being in a line as shown. The two hydrogen electrodes E and E' are mounted in a single rubber stopper which is inserted into one of the holes in the cover. One of these electrodes, E', enters the tube G of the gas lift pump L. This pump is operated by a stream of hydrogen gas which flows through the tube h_2, which enters through a stopper in the second hole in the cover. The other hydrogen electrode, E, is in the body of the solution in the vessel A. The solution is stirred, and at the same time saturated with hydrogen, by a stream of that gas through the tube h_1 which, in the actual apparatus, reaches to the bottom of the vessel A. The tip of the buret B and the gas exit tube leading to the trap T pass through the third rubber stopper. In operation pure hydrogen gas is passed through tubes h_1 and h_2 until no difference in potential is observed between the electrodes E and E'.[2] Under these conditions

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[2] In order to cause hydrogen to flow from more than one outlet at the same time about 20 cm. of 0.5 mm. capillary tubing are inserted in the lines h_1, h_2 and h_3. This tubing can be seen in Fig. 1. Without this tubing bubbles will appear at only one place unless the gas pressure is very high.

both electrodes are saturated with hydrogen, and the solution in the tube G is uniform with that in the body of the solution due to circulation through this tube caused by the gas lift pump L. Now if the stopcock S is given a turn of about 45° this gas stream is stopped, causing an isolation of the solution in the tube G from the body of the solution. A further turn of the stopcock S causes the titrating fluid to flow into the solution from the tip of the buret B. On turning the stopcock back far enough to stop the flow of fluid, but not far enough to start the gas, a potential ΔE will exist between the electrodes E and E'. This potential is due to the concentration difference between the solution in the tube G and that in the body of the solution.

As already stated it has been found necessary to have all the oxygen removed from the titrating fluid. In fact, the addition of one or two drops of an oxygen-bearing solution from the buret B, after the electrodes are saturated with hydrogen, causes a very large and rapidly changing potential to develop between E and E', quite obscuring the potentials due to hydrogen and hydrogen ions. Oxygen is kept out of the titrating solution as follows. The titrating fluid (a solution of a base in these experiments) is placed in the special flask, F. This type of flask was described in a previous paper.[1e] With the head H turned in the direction indicated, a stream of hydrogen through tube h_3 will bubble through the liquid, displacing the oxygen in the solution in the flask and saturating it with hydrogen. From the flask the gas passes through the buret B and out of the special trap R. This is designed so that the first few cubic centimeters of the gas force the water in the lower bulb into the upper one, after which the gas bubbles through the tube J. After the air is sufficiently removed from the system, the buret may be filled from the flask by turning the head H in the reverse direction to that shown in the diagram, allowing the gas to flow through h_3. The flow of gas and fluid may then be stopped by turning the head H through 90°. If the fluid is now run into the vessel A from the buret tip B, the volume of titrating fluid is replaced by hydrogen from the trap R. It is usually necessary to sweep gas out of the tip of the buret B and to reject some titrating fluid in order to start the buret reading at a convenient point. This rejected liquid is prevented from entering the solution in the vessel A by swinging the bent tube M under the buret tip by means of the trap T to which it is attached. In this position the rejected fluid will be forced by the gas stream from tube h_1 into the trap. The tube M may then be swung out of the way of the fluid from the buret.

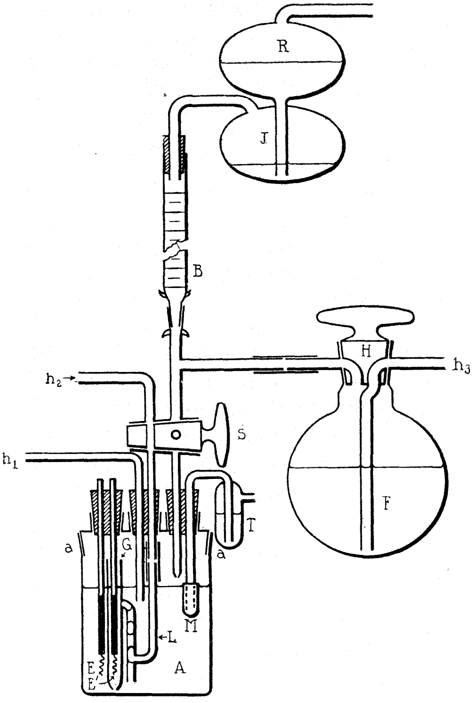

Fig. 2.

The Electrodes.—At first sight it would appear likely that, since the two electrodes are exposed to the solution under very nearly the same conditions, the readings should be independent of the purity of the hydrogen gas, because the effect of impurities, for example oxygen, would be expected to be about the same on both electrodes. Quite the contrary was found to be true. We have found it necessary to bring the hydrogen to a very high purity before the two electrodes will have the same potential with the circulating pump operating so that both electrodes are bathed with the same solution. Ordinary tank hydrogen gave differences of potential between 5 and 50 millivolts. These conditions were but slightly improved, and occasionally were made worse by passing the gas through alkaline pyrogallol. After passing over a nickel catalyst prepared as described by Latimer, Buffington and Hoenschel[3] and which, according to these authors, leaves less than 0.01% of oxygen in the gas, a difference of several millivolts between the electrodes persisted. A hot wire filament, as recommended by Lewis, Brighton and Sebastian,[4] had no perceptible effect. However, by using a reduced copper catalyst, at a relatively high temperature (650 to 700°), the two electrodes will show a zero difference of potential. The copper catalyzer used consisted of reduced copper oxide, in wire form, filling 20 cm. of a quartz tube of about 2.5 cm. diameter. To prevent channeling of this material, plugs of copper gauze were placed at the ends and at intervals in the catalyst. In order to keep out oxygen it was found necessary to avoid rubber tubing as far as possible, as the behavior of the electrodes gave definite evidence of the effect of the diffusion of oxygen through it. Such rubber connections as were unavoidable were made "glass to glass" with thick rubber tubing, impregnated with a paraffin–vaseline mixture.

The explanation of this surprising effect of very small amounts of oxygen in the hydrogen in preventing the two hydrogen electrodes from reaching the same potential is almost certainly as follows. The platinizing on the electrode tends to remove the last traces of oxygen by catalyzing its reaction with hydrogen. However, the electrode in the body of the solution in the vessel A of Fig. 2 is bathed by a constantly changing solution which is supplied with traces of oxygen from the tube h_1, and the electrode is therefore not permitted to come to equilibrium. The electrode in the tube *G*, on the other hand, is furnished with a relatively small portion of the solution which flows over it slowly. The catalysis of the reaction of the hydrogen with the oxygen has thus the opportunity to proceed further and the electrode thus reaches a potential nearer to the true equilibrium value than is possible with the electrode in the body of the solution.

The observations just described on the effect of traces of oxygen on the potentials at the electrodes appear to be important as they indicate clearly that as ordinarily used a platinized platinum electrode has, in addition to its generally recognized function of bringing the reaction between hydrogen gas, hydrogen ions and electrons to equilibrium, the responsibility of catalyzing the reaction between hydrogen and traces of oxygen, which, as we have seen, have decided influence on the potentials observed. It seems probable, therefore, that potentials measured with hydrogen electrodes which have gas flowing over them may be in error, even if constant readings are obtained, unless extraordinary precautions are taken to make certain that the hydrogen is pure.

A Test of Standards for Precise Acidimetry.—Since, as has already been stated, it has been necessary for us to know the concentrations of acid solutions to high precision, a comparison of three different standards for

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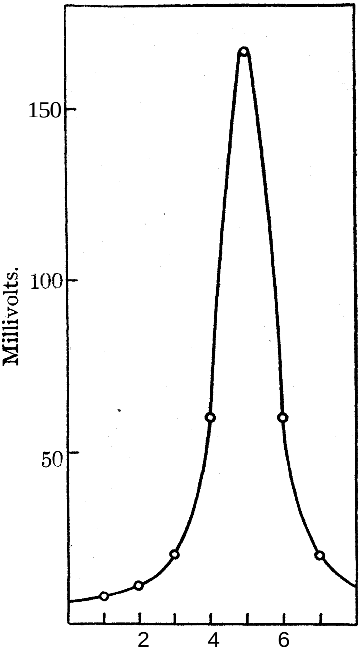
[3] Latimer, Buffington and Hoenschel, THIS JOURNAL, 47, 1571 (1925).

[4] Lewis, Brighton and Sebastian, *ibid.*, 39, 2245 (1917).

acidimetry was made, employing the electrometric method in each case to find the end-point.[5] A solution of sodium hydroxide with which the acid solutions could be titrated was prepared. The first solution of base used was calibrated, using (a) constant boiling acid, and (b) potassium acid phthalate. The constant boiling acid was prepared as described by Foulk and Hollingsworth,[6] using the slight modification of their procedure described by MacInnes and Dole,[7] who checked, very closely, Foulk and Hollingsworth's value for the composition of this material. A dilution of this acid was made by weight to approximately the concentration of the base. This diluted acid was then placed in a weight buret and about sixty grams was weighed out into the vessel A of the apparatus shown in Fig. 2. Then, from another weight buret, enough of the solution of the base, the titer of which was desired, was added to bring the acid within about 0.2 g. of neutralization. (To do this a preliminary rough titration, using phenolphthalein, was necessary.) The vessel A was put into place in the apparatus and the currents of hydrogen started through tubes h_1 and h_2. When equilibrium was established (shown by a zero or nearly zero potential between electrodes E and E') the titration was completed from the buret B, using the solution of the base diluted in the proportion one to ten. This had previously been saturated with hydrogen in the flask F. The solution from B was added usually a drop at a time and the corresponding readings of the potentials between E and E' were made. One drop is, of course, equivalent to 0.1 drop of the original solution. A typical plot of the readings thus obtained is shown in Fig. 3, the e. m. f. values in millivolts appearing as ordinates and drops of solution as abscissas. The sharpness with which the end-point can be located is shown by the fact that the last drop, representing about 0.01% of the total titer, produced in this case a potential difference of 167 millivolts, whereas the previous and following



Drops of diluted base solution.
Fig. 3.

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[5] Such comparisons, using ordinary indicators, have been made by Morey, THIS JOURNAL, 34, 1027 (1912), and by Hendrixson, *ibid.*, 37, 2352 (1915). These workers have not, however, attained quite the accuracy we have desired

[6] Foulk and Hollingsworth, *ibid.*, 45, 1220 (1923)

[7] MacInnes and Dole, *ibid.*, 51, 1119 (1929).

drops produced potentials lower than this by over 100 millivolts. The curve shown in Fig. 3 happens to be symmetrical about the maximum ordinate. In this case the drop producing this maximum potential exactly completes the titration. However, if the adjoining ordinates were of unequal heights it was possible by a simple interpolation to compute the portion of the last drop added that would have finished the titration. The interpolation was carried out with sufficient accuracy by drawing lines through the last two points on each side of the end-point, and noting the point at which they cross.

The solution of base was also standardized, using potassium acid phthalate furnished by the Bureau of Standards. We followed the directions for drying the material, and used the factor (0.9997) for its purity, as given in a circular from that Bureau. In this case the solid salt was weighed out into vessel A and the solution of the base was added from a weight buret within one or two tenths of a gram of the computed amount, after which the titration was finished as described above. The end-point was quite as definite, as in the preceding case, although the potentials were much lower. Table I, based on determinations made by the junior author, gives the results of standardizations, made by the two methods outlined above, of the solution of base. The constant boiling acid which, as collected, had a composition of 20.214% HCl was diluted in the proportion of 48.3299 grams of acid in 987.203 grams of final solution. The table is mostly self-explanatory. However, the column headed "Correction to weight of base" is computed from the weight of diluted base solution added from the buret in the final electrometric titration carried out in the apparatus shown in Figs. 1 and 2.

TABLE I

STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION BY MEANS OF CONSTANT BOILING HYDROCHLORIC ACID AND POTASSIUM ACID PHTHALATE

Standard	Weight Standard	Weight Base	Correction to weight of base	Normality of base
Constant boiling HCl	2.90026	47.2977	0.0645	0.33945
Constant boiling HCl	2.70567	44.1365	.0471	.33946
Potassium acid phthalate	4.0238	57.9822	.0990	.33948
Potassium acid phthalate	4.2204	60.7734	.1446	.33948

It will be observed that the two standards yield the same result with a high degree of accuracy. This test was repeated by an assistant, Mr. Valik, using a solution of sodium hydroxide having another strength. In this series another standard, pure benzoic acid from the Bureau of Standards, was also used. Since the addition of alcohol to dissolve this acid, as recommended by Morey,[8] has an unfavorable effect on the hydrogen electrodes and on the end-point, the following procedure, which does not involve the

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[8] Morey, THIS JOURNAL, 34, 1027 (1912); see also Weaver, *ibid.*, 35, 1309 (1913).

use of that solvent, was adopted. About 1.4 g. of the solid acid was placed in a bottle of about 100-cc, capacity and the solution of base, the strength of which was approximately known, was added within 0.1 to 0.2 g. less than the amount necessary for neutralization and the flask was tightly stoppered. With sufficient shaking all the benzoic acid went into solution. The resulting solution, which was slightly acid and would therefore not absorb carbon dioxide, was washed into the vessel A of Fig. 2, and the titration was completed electrometrically with dilute base as already described. The results obtained for the standardization of the second. solution of sodium hydroxide are given in Table 11. All weights given in these tables have been reduced to vacuum standard. The weight of the potassium acid phthalate is that of the material of 0.9997% purity. The constant boiling acid in the second series of determinations contained 20.224% of HCl.

TABLE II

STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION BY MEANS OF CONSTANT BOILING HYDROCHLORIC ACID, POTASSIUM ACID PHTHALATE AND BENZOIC ACID

Standard	Weight Standard	Weight Base	Correction to weight of base	Normality of base
Constant boiling acid	1.56523	41.2528	0.1483	0.20967
Constant boiling acid	1.56055	41.1483	.1364	.20963
Constant boiling acid	1.55804	41.1090	.1424	.20959
Potassium acid phthalate	2.1118	49.1500	.1833	.20963
Potassium acid phthalate	2.0194	47.0256	.1453	.20965
Potassium acid phthalate	2.0892	48.7370	.0684	.20963
Benzoic acid	1.4713	57.3510	.1538	.20963
Benzoic acid	1.4389	56.0079	.2263	.20965
Benzoic acid	1.4387	56.1074	.1271	.20962

It is evident from the data presented in Tables I and II that, in the first place, the electrometric method as outlined is capable of giving results of high precision, and, also, that the three methods tested for standardizing solutions of bases are equally accurate. Of these three methods the use of potassium acid phthalate is probably the most convenient. An empirical factor for the purity of the material must, however, be used. The constant boiling acid method involves a distillation which must be carefully carried out at a barometric pressure which must be constant and accurately known. Although it is hard to get into solution, benzoic acid is unquestionably the best material to use as a standard for precise acidimetry, since its use depends only on the stoichiometric relations, and no analytical results of other workers have to be accepted. Furthermore, it can be obtained in a state of highest purity.

A paper which will follow shortly will deal with the question of the equivalence of the electrometric and stoichiometric end-points, and with the titration of mixtures of acids.

Summary

1. The differential electrometric method for titration has been adapted to the use of hydrogen electrodes.

2. The usefulness of the method has been shown by its application to precise acidimetry. Three standards for use in acidimetry: constant boiling hydrochloric acid, potassium acid phthalate and benzoic acid, have been tested and have been shown to be suitable for accurate work (0.01% or better).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE PHOTOCHEMICAL INTERACTION OF ETHYLENE AND AMMONIA

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RECEIVED DECEMBER 8, 1930 PUBLISHED FEBRUARY 9, 1931

The present work had its origin in some experiments carried out by J. R. Bates at the suggestion of one of us (H. S. T.) in December, 1926, during our studies of photosensitized decompositions by excited mercury.[2] In this work it was found that, in the decomposition of ammonia, both photochemically and by excited mercury, the non-condensable gas first received in a flowing system was mainly hydrogen. This suggested a primary decomposition of ammonia into NH_2 and H, and experiments were undertaken to determine whether evidence for this could be obtained from reactions initiated by such atomic hydrogen. This was readily forthcoming, since we showed that the photochemical decomposition of ammonia in presence of hydrogen and carbon monoxide led to very much larger yields of formaldehyde than were obtained under the same arc conditions in the absence of ammonia. This latter fact was also proof that we were not producing the formaldehyde by reason of the presence of excited mercury in the system. The reaction was sufficiently rapid that a solid residue was quickly laid down on the vessel walls; the solid was assumed to be hexamethylenetetramine. We have not yet examined the reaction further, and therefore confine ourselves to recording at this time the free solubility of the solid product in water.

In the following year Hill and Vernon,[3] at Princeton, also showed that the illumination of ammonia in the far ultraviolet and at low partial pressures, in quartz vessels, in contact with tungstic oxide gave an immediate reduction to the blue oxide. This again pointed to atomic hydrogen, but not so directly, since hydrazine might have been the product to

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[1] Commonwealth Fund Fellow.

[2] Bates and Taylor, THIS JOURNAL, 49, 2438 (1927).

[3] Unpublished experiments.

which such reduction was to be attributed. Further work in this very promising field had to be postponed pending the erection of a new laboratory in which facilities were available for the development of light sources of high intensity in the region absorbed by ammonia. These were obtained last year, and the present program was then initiated.

During the latter part of 1929 an apparatus was assembled to study the sensitization of the hydrogen-ethylene reaction by atomic hydrogen produced in the photo-decomposition of ammonia. Before the release of the high tension spark sources from other work,[4] a communication by Farkas, Haber and Harteck[5] on the photosensitization of the oxidation of hydrogen and carbon monoxide by means of ammonia indicated that the field of ammonia sensitization was being pursued elsewhere. We have, therefore, utilized, in the present work, the available mercury light sources of the laboratory in continuation of the program initiated as described above.

Our choice of the ethylene–hydrogen reaction for study was dictated by several reasons. In the presence of excited mercury the reaction has been very fully investigated,[6] and the various possible reactions identified. The reactions are fast, and their progress can be followed manometrically. With oxygen as one of the reactants in the system, there is always the possibility that the primary interaction of ammonia with oxygen might influence the results. The deposition of solid products in the hydrogen–carbon monoxide reaction ascertained in the first experiments was the principal factor in our choice of the hydrogen–ethylene reaction. We anticipated straightforward gas reactions in the case of hydrogen and ethylene but our experiments have shown that the deposition of liquid products is the principal reaction, and these inhibit, in part, the reactions occurring.

We shall present first the nature of the experimental procedure and the experimental results. A general discussion of the data obtained will then be given.

Experimental Details

Ethylene was prepared by washing the gas from a cylinder with sulfuric acid and condensing in liquid air, dissolved non-condensable gases being then removed by melting in vacuum, freezing, and re-evacuating. Approximately one-quarter of the condensate was pumped off at its melting point, and the bulk of the liquid was then distilled at −100° in vacuum directly into the storage globe. Ammonia was prepared similarly, the gas from a cylinder being frozen in liquid air, freed from dissolved gases and a middle fraction collected by distilling from a bath at −100°. Commercial electrolytic hydrogen was purified by passing over heated platinized asbestos, and drying with phosphorus pentoxide. Gas mixtures were prepared by admitting the gases in turn into the previously evacuated reaction vessel up to the required pressure, as indicated by a mercury manometer.

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[4] Kistiakowsky, THIS JOURNAL, 52, 1868 (1930).

[5] Farkas, Haber and Harteck, *Naturwissenschaften*, 12, 267 (1930).

[6] Taylor and Hill, THIS JOURNAL, 51, 2922 (1929).

The mercury arc was of the vertical type, uncooled and normally operated at about 2.5 amp. from the 110-volt d. c. circuit. The region absorbed by ammonia lies almost at the limit of transmission of quartz, and the available radiation of this wave length was found to fluctuate from one experiment to another. For this reason the results of different experiments cannot, in general, be compared with one another. In some cases, however, as, for example, in the comparison of the decomposition of ammonia with and without ethylene, comparable conditions were maintained for two sets of observations.

Two reaction vessels were employed. **A** cylindrical bulb of quartz (Vessel **A)** 16 cm. long by *2.5* cm. diameter was used when temperature conditions were of secondary importance. It was illuminated from one side by the vertical arc. Reaction vessel B was an annulus of quartz, of 7.5 cm. external diameter, 4.5 cm. internal diameter and 10.5 cm. long, which was immersed in a constant-temperature water-bath and illuminated by a vertical arc placed co-axially within the annulus. The reaction vessels were cleaned between successive experiments by evacuating, filling with oxygen, and heating to a red heat. The film of oil deposited during the reaction was completely removed in this way.

Experimental Results

General Course of the Reaction.—A mixture of ethylene and ammonia when illuminated in quartz reaction bulb A, with the mercury arc placed at a distance of 1 cm., showed a steady decrease of pressure, the reaction being followed by interrupting the illumination, and measuring the pressure with the bulb immersed in a bath at 20° and in liquid air. Such a series of observations is recorded below.

TABLE I

PRESSURE VARIATION ON ILLUMINATION OF 10.05 CM. OF ETHYLENE AND 2.23 CM. OF AMMONIA

Time of illumination	Total pressure, cm.	Pressure of non-condensable gas (corrected to 20°), cm.
0 Minutes	12.28	0.00
25	9.32	.16
50	7.45	.00
80	5.95	.39
105	5.17	.58
170	4.45	.80
316	4.38	1.54
496	4.50	1.71
760	4.72	2.15
27 Hours	5.13	2.77
32'	5.62	3.25
34 5	5.87	3.89
62 5	6.07	4.05

[a] At this point the position of the arc was shifted to the opposite side of the reaction vessel, and its distance altered from 1 cm. to 0.5 cm.

As the reaction progressed a light brown oil was deposited, which was found to retard the reaction, due, probably, to a reduction of the effective light intensity. This is shown by the following measurements. An ethylene–ammonia mixture ($p_{C_2H_4}$, 9.97 cm.; p_{NH_3}, 10.45 cm.) was illuminated for 160 minutes, and gave a pressure reduction of 2.84 cm. After evacuating the reaction bulb (the oil not being appreciably volatile), a fresh gas mixture was admitted ($p_{C_2H_4}$, 9.80 cm.; p_{NH_3}, **10.21** cm.). Continuing the illumination under the same conditions, the decrease in pressure in fifty minutes was only **0.24** cm. Moreover, the reaction rate at the beginning of the second experiment was approximately the same as that at the point where the first was interrupted.

On illuminating ammonia in the reaction vessel in which an ethylene–ammonia mixture had reacted with a pressure reduction of 1.86 cm., the ammonia decomposition resulted in a pressure increase of 0.07 cm. in ten minutes, whereas the average value for ammonia under the same conditions in a clean vessel was **0.24** cm. in ten minutes, showing that the oil also retarded the decomposition of ammonia.

Illumination of Ethylene Alone.—On illuminating ethylene alone with the mercury arc in vessel A illuminated at 1 cm. distance there was a reaction, the rate of decrease of pressure being approximately 20–30% of that observed with ammonia present. This is shown by the following measurements.

TABLE II

COMPARISON OF PHOTOCHEMICAL ACTION WITH AND WITHOUT AMMONIA

$p_{C_2H_4}$, cm.	p_{NH_3}, cm.	Time of illumination, min.	Pressure decrease, cm.
30.53	..	45	1.97
33 22	6.66	45	6.17
17.87	..	30	0.63
18.01	3.68	30	4.14

With a hot arc this reaction cannot be due to a mercury sensitized reaction, and probably represents a direct polymerization following absorption by the ethylene itself. Using reaction vessel B the polymerization of ethylene without ammonia becomes inappreciable. Thus, with this vessel and with $p_{C_2H_4} = 14.64$ cm.. the pressure decrease on illuminating for **140** minutes was **0.12** cm.; with $p_{C_2H_4} = 32.57$ cm., the pressure decrease on illuminating for ninety minutes was **0.10** cm.

In experiments with reaction vessel A the reaction of ethylene alone was neglected, these runs being made mainly in the investigation of the products of the reaction. Reaction vessel B was used in studying the kinetics of the reaction, and in that case the reaction of ethylene alone was some 5% of that in the presence of ammonia.

Formation of Saturated and Unsaturated Hydrocarbons in the Reaction.—To determine whether saturated hydrocarbons were formed in the course of the reaction, an ethylene–ammonia mixture was illuminated in vessel A and the non-condensable gas pumped off with the bulb immersed in liquid air. The residue was then distilled in vacuum into a bulb containing gas-free **10%** sulfuric acid to absorb ammonia and amines. The moist residue was returned to the reaction vessel and the pressure remeasured. The percentage of unsaturated hydrocarbon in this residue was then determined by absorption with fuming sulfuric acid. Where the quantity of gas was sufficient, a sample was pumped off and oxidized over copper oxide heated to a red heat, the increase in pressure on oxidation and the decrease on treating the residue with potash giving the number of carbon atoms in the molecule. Two experiments were also made in which hydrogen was introduced to determine whether this caused an increase in the amount of saturated hydrocarbon formed. These results are recorded below. Those in which hydrogen was present are discussed later.

TABLE III

FORMATION OF SATURATED AND UNSATURATED HYDROCARBONS

	$p_{C_2H_4}$	p_{NH_3}	p_{H_2}	Δp in reaction, cm.	Time, hours	% of residual gas absorbed by fuming H_2SO_4	Carbon value
1	38.80	6.17	...	10.88	10.5	94	...
2	32.67	5.47	...	12.11	15	93	2.0
3	24.72	7.00	11.89	11.12	16	89	...
4	30.33	8.33	13.73	12.01	15	93	2.1
5	33.68	5.92	...	12.18	5.25	92	...

These results show that in the course of the reaction a small amount of gas not absorbed by fuming sulfuric acid was formed, which must be saturated hydrocarbon. It is very probable that this residue consists of ethane. The approximation of the carbon value for the total residue to the value C_2 shows that the residue contained no appreciable amounts of the higher homologs of ethylene—it must have consisted in the main of unchanged ethylene.

Influence of Hydrogen on the Reaction.—The mercury sensitized reaction between ethylene and hydrogen was proved not to occur under the conditions of illumination used by radiating an ethylene–hydrogen mixture (p_{H_2}, 15.66 cm.; $p_{C_2H_4}$, 5.43 cm.) in the reaction vessel B. Mixtures of ethylene, hydrogen and ammonia were next illuminated in the simple cylindrical bulb to determine if, under these conditions, the hydrogen reacted, the hydrogen pressure being measured before and after each run by immersing the reaction bulb in liquid air.

TABLE IV

INFLUENCE OF HYDROGEN ON THE REACTION

	p_{H_2}, cm.	p_{NH_3}, cm.	$p_{C_2H_4}$, cm.	Time, min.	Total Δp, cm.	Initial p_{H_2} at −180°, cm.	Final p_{H_2} at −180° cm.
1	10.06	2.34	10.05	72	−4.09	3.29	3.41
2	10.06	10.03	10.08	38	−2.43	3.36	3.34
3	20.12	9 90	10 09	97	−8.53	6.98	6.97

From the last two columns it is evident that the amount of hydrogen used in the reaction is negligible. Further support for this conclusion is obtained from the analyses recorded above, where it was shown that, in presence of hydrogen, there was no difference in the amount of saturated hydrocarbon formed.

Reaction of Ammonia.—In the presence of ethylene, ammonia might be expected either to undergo its normal decomposition into nitrogen and hydrogen, or to react with the hydrocarbon, giving amines as the main product. To determine the extent to which the normal decomposition occurred, ammonia was illuminated in the quartz reaction bulb A with the mercury arc for a definite time and the amount of non-condensable gas formed determined by immersing the bulb in liquid air at the end of the run. An ethylene–ammonia mixture with the same pressure of ammonia was then illuminated for the same time under identical conditions, and the non-condensable gas again determined.

TABLE V

AMMONIA DECOMPOSITION WITH AND WITHOUT ETHYLENE

	p_{NH_3}, cm.	ΔP, cm.	Time of illumination, min.	$p_{l.a.}$, cm.	p_{NH_3}, cm.	$p_{C_2H_4}$, cm.	ΔP, cm.	Time, min.	$p_{l.a.}$, cm.
1	5.17	+1.42	45	1.02	5.03	14.75	−5.38	50	0.05
2	4.95	1.30	40	0.76	5.11	15.26	..	40	.03
3	10.00	0.95	63	.65	10.03	15.00	−4.29	63	− .01

The readings under $p_{l.a.}$ refer to the pressure of non-condensable gas at liquid air temperatures. Other pressure measurements were made at 20°. These readings show that in the presence of ethylene the simple decomposition of ammonia was reduced to less than 10% of its normal value.

The second possibility, namely, the formation of a simple compound, should be indicated by a definite relation between the amount of ammonia which would normally have decomposed under the conditions of illumination used, and the amount of ethylene used. The total decrease in pressure in the reaction has been used as a measure of the latter quantity; actually this measures the minimum value of this quantity, for the true pressure decrease will be reduced by the formation of other volatile products (such as amines, and saturated and unsaturated hydrocarbons).

A series of observations of this type was conducted in reaction vessel B maintained at room temperature. The ammonia decomposition rate was first determined over a period of forty to eighty minutes, the residue being then pumped out and an ammonia–ethylene mixture introduced, the arc conditions remaining unchanged. The decrease in pressure over the first ten to twenty minutes was determined, this short period of illumination minimizing the error due to the accumulation of oil.

The average value of r is 5.0. This measures the ratio of the pressure decrease in presence of ethylene to the pressure increase due to the simple ammonia decomposition. That is, for every one molecule of ammonia which would have decomposed, at least five molecules of ethylene disap-

TABLE VI

AMMONIA DECOMPOSITION WITH AND WITHOUT ETHYLENE

	p_{NH_3}	Δp in 10 minutes, cm.	p_{NH_3}	$p_{C_2H_4}$	Δp in 10 minutes, cm.	r
1	4.77	0.095	4.86	15.15	−0.42	4.4
2	5.03	.098	5.06	15.15	− .46	4.7
3	5.08	.085	5.00	15.15	− .44	5.2
4	5.05	.052	5.00	15.13	− .28	5.4
5	5.05	.049	5.11	15.07	− .235	4.8
6	4.95	.045	5.07	15.07	− .245	5.4

pear. The high value of this ratio is strongly against the formation of a simple compound, such as a volatile amine. Even for a tertiary amine the ratio would be only 3, and it appears very probable that the ethylene has undergone a polymerization, resulting in the deposition of the non-volatile oil.

As a further check on the disappearance of ammonia in the reaction, four runs were made in which the residual ammonia (+ amines) was determined, after varying times of illumination, by admitting 1–2 cc. of 30% sulfuric acid directly into the reaction vessel from a side tube, the observed decrease in pressure being corrected for the vapor pressure of the acid.

TABLE VII

RESIDUAL AMMONIA (OR AMINES) AFTER ILLUMINATION

	p_{NH_3}	$p_{C_2H_4}$	Time of illumination, min.	Δp, cm.	Gas absorbed as % of original ammonia
1	5.50	19.59	30	− 3.71	96
2	5.25	19.93	60	− 5.30	92
3	5.75	19.95	120	− 9.20	78
4	5.62	19.76	210	−11.68	62

If a part of the ethylene had formed a volatile amine, then, for every ammonia molecule decomposed, one molecule of amine should have been formed, and the gas absorbed by sulfuric acid should have remained constant throughout a run. The above table shows that such is not the case; that is, volatile amine formation must have occurred to a very much smaller extent, if at all.

Finally, an attempt was made to determine whether the amount of ammonia decomposed in the presence of ethylene was the same as that which would be observed on illuminating ammonia alone under the same conditions. Ammonia was first illuminated, the pressure change in a definite time being measured. An ethylene–ammonia mixture was then illuminated under the same conditions, and for the same time, and the residual ammonia determined by introducing 10% sulfuric acid directly into the reaction bulb. The following values were obtained.

These results show that within the probable error of the experiments the ammonia decomposition proceeded normally in presence of ethylene,

TABLE VIII

AMMONIA DECOMPOSITION WITH AND WITHOUT ETHYLENE

	Pressure of ammonia decomposed measured by pressure change, ethylene absent, cm.	Measured by absorption ethylene present, cm
Expts. Ia and b	0.79	0.93
Expts. IIa and b	1.00	.80
Expts. IIIa and b	1.08	.97

the products of the reaction alone being different. The non-condensable gas formed in the reaction was pumped off in two experiments, and analyzed for hydrogen and nitrogen by burning over copper oxide. With $p_{C_2H_4}$ = 15.01 cm., p_{NH_3} = 10.05 cm., and with a pressure decrease of 10.36 cm. in the reaction, the pressure of non-condensable gas formed, measured at liquid-air temperatures, was 0.33 cm., and 84% was found to be absorbed by heated copper oxide. In a repetition of this run the value 83% was obtained

The oil deposited during the reaction was not available in sufficient quantity for further examination. It was insoluble in water and acids, and soluble with difficulty in ether. A similar oil was formed in the polymerization of ethylene sensitized by excited mercury.[6] In the present case, however, it is impossible to account for the nitrogen from the decomposed ammonia except by supposing it to be present in the oil in the form of compounds of low volatility. Vapor pressure measurements made on the residue in the reaction bulb after pumping off all gas volatile at −100 to −90° were as follows.

TABLE IX

VAPOR PRESSURES OF OILY RESIDUE

Temperature, °C.	−76	−58	−44	−30
V. p., cm.	0.05	0.10	0.19	0.34

It is obvious that such measurements have minor value since the residue is undoubtedly complex. We believe the evidence presented indicates polymerization of the ethylene with the participation of the NH_2 radical at some stage of the total process later than the first stage, since this would involve volatile amine production.

Reaction Kinetics

Influence of Ethylene Concentration on the Reaction Rate.—These experiments were made in vessel B at room temperatures. A measured pressure of ammonia was admitted to the bulb, and then a small pressure of ethylene, the decrease in pressure on illumination for ten minutes being determined. After introducing a further quantity of ethylene the rate was re-determined, and so on for a series of ethylene pressures. The retardation of the reaction due to the deposition of oil was determined by working with fixed amounts of ethylene and ammonia, and measuring the pressure at ten-minute intervals (Expt. 1). By comparing this set of readings with those in which the ethylene concentration was varied, it was possible to determine if the latter had any influence on the rate.

TABLE X

INFLUENCE OF ETHYLENE CONCENTRATION ON REACTION RATE

Expt. 1. $p_{C_2H_4}$, 32.47 cm. p_{NH_3}, 5.17 cm.

Time, min.	10	20	30	40	50	60
Δp in 10 min., cm.	−0.26	−0.30	−0.24	−0.23	−0.22	−0.20

Expt. 2. p_{NH_3}, 4.98 cm.

$p_{C_2H_4}$, cm.	4.7	9.35	14.4	19.1	28.3
Δp in 10 min., cm.	−0.44	−0.42	−0.40	−0.38	−0.38

Expt. 3. p_{NH_3}, 10.03 cm.

$p_{C_2H_4}$, cm.	1.0	4.4	9.6	22.3
Δp in 10 min., cm.	−0.27	−0.24	−0.29	−0.26

Expt. 4. p_{NH_3}, 18.8 cm.

$p_{C_2H_4}$, cm.	0.9	2.3	5.25	13.9
Δp in 10 min., cm.	−0.12	−0.12	−0.10	−0.14

These results show that over a wide concentration range the rate of reaction is independent of the ethylene pressure.

Influence of Ammonia Concentration on the Reaction Rate.—The same method was used in studying the influence of ammonia concentration on the reaction rate, a fixed pressure of ethylene being used while the ammonia concentration was varied. As the reaction progressed the ethylene concentration decreased, but it has already been shown that this does not influence the rate. Similarly, in the previous set of observations, the ammonia concentration must have decreased; this effect has been neglected, a course which is justified by the results given below.

TABLE XI

INFLUENCE OF AMMONIA CONCENTRATION ON REACTION RATE

Expt. 1. $p_{C_2H_4}$, 20.99 cm.

p_{NH_3}, cm.	0.9	3.1	9.0	12.0
Δp in 10 min., cm.	−0.13	−0.22	−0.22	−0.18

Expt. 2. $p_{C_2H_4}$, 10.03 cm.

p_{NH_3}, cm.	0.3	0.8	1.8	4.4	9.6
Δp in 10 min., cm.	−0.08	−0.15	−0.21	−0.19	−0.20

Expt. 3. In this experiment the ammonia was introduced as a mixture with hydrogen containing 16% of ammonia. $p_{C_2H_4}$, 10.08 cm.

p_{NH_3}, cm.	0.04	0.12	0.22	0.38	1.14
Δp in 10 min., cm.	−0.05	−0.08	−0.11	−0.13	−0.18

These results show that above a certain pressure the rate of reaction is independent of the ammonia pressure. This pressure is approximately equal to 1.5 cm., and may be interpreted as being the pressure at which the active light is completely absorbed. Below this point the reaction rate increases with increasing ammonia concentration, but the accuracy of the measurements does not justify any attempt to formulate a relation between the two.

Temperature Coefficient of the Reaction.—The approximate temperature coefficient of the reaction was determined by working with reaction vessel B placed in a water-bath which could either be maintained at 15° or heated at 98°. The radiation emitted by the arc was found to be very sensitive to temperature for the wave length region absorbed by ammonia, and the decomposition of ammonia itself, for which the temperature coefficient is known, was used as a method of calibration. The ammonia decomposition was found to have an apparent temperature coefficient of 3.1 for a temperature increase of 83°. From Kuhn's value of 1.05 per 10°, the factor should be 1.4. Taking this discrepancy as due to a change in the condition of the arc, the observed values for the temperature coefficient (of the ethylene–ammonia reaction) were divided by the factor $3.1/1.4 = 2.2$, to give the true values.

Ammonia Decomposition.—In a series of runs in which the pressure of ammonia was varied from *3* cm. to 18 cm., the following values were obtained for the ratio of the decomposition rate at 98° to that at 15°: 3.4, 3.7, 3.9, 2.4, 3.9, 2.9, 2.8, 2.4, 2.7; average, 3.1.

Ethylene–Ammonia Reaction.—The following measurements were made with ethylene–ammonia mixtures, the reaction vessel being cleaned and the arc reset between the measurements at the two temperatures.

15°				98°				
p_{NH_3}, cm.	$p_{C_2H_4}$, cm.	Δp, cm.	Time, min.	p_{HN_3}, cm.	$p_{C_2H_4}$, cm.	Δp, cm.	Time, min.	r
3 03	15 **13**	−0.94	30	3.09	14 94	−2.48	30	**2.64**
5 08	15.24	−1.29	40	5.05	15.40	−2.03	25	**2.52**
5 41	15.05	−1.67	60	5.40	14 96	−1.85	20	**3.33**
5.02	15.10	− 186	60	5.05	15.05	−1.90	20	**3.06**

The value of r in the last column is the ratio of the pressure decrease at 98° to that at 15° calculated for equal times of reaction.

The average value of r is 2.9, **i.** e., dividing by the factor 2.2, the temperature coefficient for 83° is 1.32 or 1.04 per 10°. Taking into account the low degree of accuracy of the determinations, this value does not differ sensibly from that for the photo-decomposition of ammonia.

Discussion of Results

A survey of the data obtained in the preceding sections justifies the general conclusion that the photochemical decomposition of ammonia induces the low-temperature polymerization of ethylene. We ascribe this induced polymerization to the liberation, in the reaction system, of atomic hydrogen formed in the decomposition of ammonia. At some stage in the process, however, the nitrogen fragment of the dissociation enters the reaction and is removed not as a volatile amine, but as a liquid, non-volatile, nitrogen carbon compound of undetermined composition.

The polymerization of ethylene with the aid of atomic hydrogen is a familiar process by reason of earlier work on excited mercury. In the latter case, however, polymerization is always accompanied by hydrogenation, which, with hydrogen-rich mixtures, may even be practically the exclusive reaction.[6] This result is in striking contrast to the present work with ammonia as the source of atomic hydrogen. Here we find the hydrogenation occurring to be of the order of 20% of the ethylene polymerized. It is evidently necessary, therefore, to account for such a divergence of behavior. The reaction with ammonia is as much a process of polymerization as that found by Taylor and Jones,[7] in which ethyl radicals liberated from decomposing metal ethyls in mixtures of hydrogen and ethylene at 250° produced mainly ethylene polymers with only small amounts of saturated hydrocarbons.

Experimentally, the outstanding divergence between the processes with ammonia and with mercury is probably associated with the concentration of atomic hydrogen produced. In the case of mercury, as has frequently been pointed out, the reaction volume is mainly confined to a very thin element of volume adjacent to the vessel surfaces receiving illumination by resonance radiation, owing to the extremely high absorption coefficient of mercury atoms for this light. Comparatively, in the case of ammonia, the concentration of atomic hydrogen produced is very much less.

That saturated hydrocarbon formation is small with ammonia in hydrogen–ethylene mixtures at room temperatures and is subordinate with metal alkyls even at 250° suggests definitely that a reaction $C_2H_5 + H_2 = C_2H_6 + H$,[8] postulated in earlier communications[2,6] on this subject to account for ethane formation, must in reality be a reaction of low collision efficiency. This conclusion is in agreement with a wide variety of experience accumulated in the past year,[4,9,10,11] concerning the reactivity of the atoms and radicals, O, Cl, F, CHO with hydrogen molecules. The formation of hydrogen peroxide to the exclusion of water at ordinary temperatures from atomic hydrogen and oxygen molecules[2] also points to the inefficiency of collisions in the process, $OH + H_2 = H_2O + H$. We are led, therefore, to reject the reaction $C_2H_5 + H_2 = C_2H_6 + H$ as the process producing saturated hydrocarbon at ordinary temperatures. At 250° and higher

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[7] Taylor and Jones, THIS JOURNAL, 52, 1111 (1930).

[8] The production of ethyl from hydrogen atoms and ethylene is an association reaction $H + C_2H_4 = C_2H_5$ to be achieved by means of a three-body process

[9] Frankenburger, *Z. Elektrochem.*, 36, 767 (1930).

[10] Farkas, Haber and Harteck, *ibid.*, 36, 714 (1930).

[11] Franck and Rabinowitsch, *ibid.*, 36, 794 (1930).

such a process may have a measurable efficiency. Even there, however, it must play a subordinate role to processes of polymerization involved in collisions between C_2H_5, C_4H_9, etc., and unsaturated molecules, $C_2H_5 + C_2H_4 = C_4H_9$. Such association reactions must be three-body processes to produce stabilized products. They are, however, more frequent than another three-body process producing amine $C_2H_5 + NH2 = C_2H_5NH_2$, owing to the high concentration of C_2H_4 compared with that of NH_2. This accounts for the absence of the lower volatile amines in the gas phase, a circumstance which is aided by the fact that such amines are themselves photochemically decomposed. The presence of nitrogen compounds in the liquid deposit indicates, however, that processes such as $C_nH_{2n+1} + NH_2 \longrightarrow C_nH_{2n+1}NH_2$ occur at later stages in the polymerization processes.

There remains the problem as to the mechanism of saturated hydrocarbon formation in excited mercury systems at ordinary temperatures. If we exclude the reaction $C_2H_5 + H_2 = C_2H_6 + H$ for reasons already set forth, we are left with the following possibilities already discussed in an earlier communication,[6] (a) $C_2H_4 + H_2 + H = C_2H_6 + H$ and (b) $C_2H_5 + C_2H_5 = C_2H_6 + C_2H_4$, together with one additional possibility not hitherto noted, (c) $C_2H_5 + HgH = C_2H_6 + Hg$. Concerning these we can make the following additional observations in the light of the new results. A reaction of type (a) should occur equally efficiently with a hydrogen atom from an ammonia molecule as with one from excited mercury and hence, in view of our experimental data with ammonia indicating low conversion to saturates, is to be considered of minor importance. Reactions of the type (b) and (c) are only to be expected in regions of high concentration of atoms or the resultant radicals and thus may be anticipated in the mercury systems and not in the ammonia system. It is to be noted that reaction (b) is a strongly exothermic process involving the evolution of some 70 kg. cal.,[12] with probably a very low activation energy. That both reactions (b) and (c) are bimolecular and are not association reactions gives them a higher degree of probability than similar reactions of two radicals involving three-body processes, e. g., $C_2H_5 + C_2H_5 + X = C_4H_{10} + X$.

Summary

The photochemical decomposition of ammonia in the presence of ethylene or ethylene–hydrogen mixtures induces a polymerization of the ethylene, even at room temperatures, to form a liquid product.

The formation of saturated hydrocarbons in the reaction system with varied ratios of hydrogen to ethylene is subordinate to the polymerization process.

The presence of ethylene reduces the formation of nitrogen and hydrogen from photo-decomposition of the ammonia. The nitrogen content of the

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[12] Mecke, *Z. Elektrochem.*, **36.** 595 (1930).

ammonia decomposed must be present mainly in the oil produced, in the form of compounds of low volatility.

The velocity of reaction is independent of the ethylene pressure over a wide concentration range and of the ammonia pressure when light absorption is complete.

The temperature coefficient of the total process is determined by that of the photo-decomposition of ammonia.

The experimental results lead to definite conclusions with regard to the efficiency of various possible methods of producing saturated hydrocarbons from ethylene and atomic hydrogen.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 256]

AN EFFECT OF THE BREADTH OF JUNCTION ON THE ELECTROMOTIVE FORCE OF A SIMPLE CONCENTRATION CELL[1]

BY GEORGE SCATCHARD AND T. F. BUEHRER

RECEIVED DECEMBER 8, 1930 PUBLISHED FEBRUARY 9, 1931

It is generally assumed that the electromotive force of a simple concentration cell, such as M, MX(m_1), MX(m_2), M, is independent of the method of making the junction between the two solutions, and that this fact has been demonstrated both theoretically and experimentally. The same theoretical argument may be extended to any cell involving a liquid junction to show that the electromotive force is independent of the thickness of the boundary layer provided that any element of the solution may be duplicated by taking x parts of the solution surrounding one electrode and $(1 - x)$ parts of that surrounding the other electrode.[2] Such a boundary is known as a "mixture boundary" and is obtained in practice when the boundary is made without diffusion. A simple concentration cell must always give a "mixture boundary" regardless of diffusion.

The electromotive force of a cell with electrodes reversible to the k'th ion, when the temperature and pressure are constant throughout the cell, is given by

$$E = \sum_{i=1}^{n} \int_B^A t_i \mathrm{d}E_{ik} = \frac{RT}{F} \sum_{i=1}^{n} \int_B^A t_i \,\mathrm{d} \ln \frac{(m_i\gamma_i)^{1/z_i}}{(m_k\gamma_k)^{1/z_k}}$$

where R is the gas constant, T the absolute temperature, F the faraday, t_i is the transference number of the i'th type of ion, z_i is its valence (taken negative for a negative ion), m_i its molality, and γ_i its activity coefficient.[3]

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[1] Presented before the Physical and Inorganic Chemistry Section at the Cincinnati Meeting of the American Chemical Society, September 10, 1930.

[2] P. Henderson, *Z. physik. Chem.*, 59, **118** (1907); 63, 325 (1908).

[3] P. B. Taylor, *J. Phys. Chem.*, 31, 1478 (1927).

A is the solution surrounding one electrode and B that surrounding the other. E_{ik} is the electromotive force of a cell without liquid junction with one electrode reversible to the i'th ion, the other to the k'th ion. Although the "individual ion activities" appear in the second part of the equation, their use is only formal for they appear in such a way that they may always be replaced by the mean activity of some salt, or by the difference in mean activities of two salts. This is shown sufficiently by the fact that in the first expression they are reduced to the electromotive forces of realizable cells. For a mixture boundary each m, and therefore the composition, is a function only of x. If the mobilities and activity coefficients are functions of the composition, independent of its gradient, they are also functions of x, and the integral is single-valued. That is, for any cell the electromotive force is independent of the thickness of the junction for a mixture boundary, and for a simple concentration cell it is independent of the method of making the boundary.

We believe that the flowing junction gives a "mixture boundary" not over 0.01 cm. in breadth, and that the Clark type of junction,[4] when properly made, also gives a "mixture boundary," but about 1 cm. broad. If so, they should give equal electromotive forces for any pair of solutions if the conditions given above are fulfilled. However, when one solution is saturated potassium chloride and the other 1 M hydrochloric acid, the difference between the two types of junction is about 0.5 mv.[5] We therefore undertook the study of a simple concentration cell to attempt to determine whether this is due to one type failing to give a "mixture boundary" or to a failure of real junctions to meet the other conditions of the thermodynamic equation. In a simple concentration cell it is not possible to obtain a difference in concentration comparable to that of the potassium or hydrogen ion in the above cell. We considered, however, that the cell Hg, HgCl, HCl (m_1), HCl (m_2), HgCl, Hg might give a measurable effect because of the large difference in the mobility of the ions. And we did find a small but indubitable effect.

Materials and Apparatus

The measurements were made in the flowing junction apparatus previously described,[6] and the junction was allowed to increase in breadth by diffusion on standing after the flow was stopped. The calomel half-cells were the same as there pictured except that the end of the goose-neck arm was sealed off, instead of being constricted, and a hole about one millimeter in diameter was blown in the perpendicular side of the tube a few milli-

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[4] W. M. Clark, "The Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, Maryland, 1928, p. 296.

[5] H. W. R. Biers, Thesis, M. I. T. (1927), confirmed by our own measurements.

[6] G. Scatchard, THIS JOURNAL, 47, 696 (1925).

meters from the end. The glass around the edge of this hole projected slightly, but not enough to prevent passing the tube easily through a rubber stopper. This simple device reduced considerably the entry of air bubbles into the goose neck. Of course, any dipping electrode should be used only where the solutions inside and out are the same.

The materials were prepared and purified as in the previous paper, except that each acid solution was boiled and cooled in a stream of nitrogen, and the composition was determined by a gravimetric chloride analysis; the calomel–mercury paste and the cell solutions were equilibriated for twelve hours on a shaking machine in an atmosphere of nitrogen, and introduced into the half cells in the absence of air. These precautions were rather more harmful than helpful, for it was not found possible to keep oxygen excluded from such half-cells, with their openings often exposed to the air, so that the cells did not give a constant electromotive force over a period of days. The absolute values of the cell potentials are therefore uncertain to several tenths of a millivolt. Probably the variations during a day's run would also have been somewhat smaller without this precaution.

The Results

Measurements were made with three sets of cells. The average results are given in Table I, where the first two columns give the concentrations of the two solutions in moles per 1000 g. of water; the third the average electromotive force in millivolts when the flow was stopped; the fourth gives the average increase of electromotive force, also in millivolts, when the solutions were flowing and the probable error of the average; the last gives the number of measurements of ΔE. About half these measurements were made on starting the flow and half on stopping it. For the latter the first measurements were made about one minute after the flow was stopped. Within the experimental error the change was complete within this time, and the electromotive force then remained constant for hours.

TABLE I

HYDROCHLORIC ACID CONCENTRATION CELLS AT 25°

m_1	m_2	E (stop)	ΔE (flow)	No. of observations
7.29	0.1047	238.0	0.028 ± 0.005	22
7.29	.01117	331.0	.058 ± .019	17
1.091	.01117	194.7	.005 ± .019	6

The averages are given to 0.001 mv. although the individual measurements were made generally only to 0.01 mv. and never beyond 0.005 mv. All conditions must be kept very constant to maintain the electromotive force of a cell constant to a hundredth of a millivolt. Perhaps our conclusions are better shown by a single run of somewhat more than six hours' duration when conditions were very good. The run was with the first cell, and E' is the observed electromotive force minus 237.00 mv. The values given are the minimum and maximum readings during a period of flow or of

TABLE II

HYDROCHLORIC ACID CONCENTRATION CELL. RUN NO. 6

$E' = E - 237.00$

Time from start		Flowing		Stopped	
Init.	Final	Min.	Max.	Min.	Max.
0	19	0.88	0.89		
20	204			0.85	0.86
205	229	.88	$.88_5$		
230	302			.84	.85
304	336	.89	.89		
338	368			.85	$.85_5$

cessation of flow. During six hours the value flowing varied only 0.01 mv. and that stopped varied only 0.02 mv. The difference between the minimum flowing value and the maximum stopped value is 0.02 mv. There can be no doubt of the reality of the effect.

From the Debye–Hückel interionic attraction theory we should expect that both the activity coefficients and the mobilities should depend slightly upon the concentration gradient, but we would scarcely expect to obtain a sufficient gradient in practice to show a measurable effect. There is another effect which should appear with much smaller gradients. Although the process is carried out in a thermostat, it cannot be isothermal. The mechanical mixing of the two solutions gives a heat effect and a resultant change of temperature in the boundary layer. These effects tend to be increased by the diffusion of ions through the boundary due to their Brownian motion. The temperature difference is dissipated, both along the axis of the tube and transversely to the walls, by the Brownian movement of all the molecules including those of the solvent. The temperature difference will be a complicated function of the concentration gradient and the time, and the effect on the electromotive force might be expected to be even more complicated and also to depend to a greater extent upon the ratio of the concentrations. Qualitatively the effect should depend upon the concentration as do our experiments. The fact that it disappears so rapidly shows that it must be very small except for a very steep gradient. Although the equation given above applies strictly to constant temperature, and therefore only to an infinitely wide boundary layer, the deviations must be immeasurably small for a breadth of even less than a millimeter.

Practically the effect of a sharp boundary in this cell is so small as to be negligible for all except the most precise work. Our results do show that a broad boundary, made by mixing rather than by diffusion if there are two electrolytes involved, should be preferable to **a** sharp boundary.

Summary

The electromotive force of hydrochloric acid concentration cells was found to increase a few hundredths of a millivolt when the liquid junction was made very thin.

A probable cause is the change in temperature at the boundary produced by the heat of mixing of the two solutions.

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THE ACTIVATION ENERGY OF ADSORPTION PROCESSES

BY HUGH S. TAYLOR

RECEIVED DECEMBER 13, 1930 PUBLISHED FEBRUARY 9, 1931

The rapid development, during the last decade, of the experimental study of adsorption phenomena at solid surfaces having catalytic activity has served to emphasize those adsorption processes in which a high degree of specificity is manifest. This work has centered attention on the operation of valence forces in determining adsorption and has indicated the existence of adsorption processes not markedly different from chemical reactions. The accumulation of experimental material has yielded, however, a number of data which, from the standpoint of classical adsorption theory, are abnormal. There has been considerable discussion of types of adsorption and distinctions drawn between "primary" and "secondary" adsorption.[1] In other cases there has been a tendency to speak of "reversible" and "irreversible" adsorption and to recognize only the former as conforming to true adsorption, to ignore the latter in the theoretical treatment of the subject. This latter attitude[2] undoubtedly arose from the lack of a general theory applicable to all types of adsorption. At the same time, owing to the orientation of experimental work, the data in conflict with the simplified theoretical treatment have grown so rapidly that it may now be stated that the experimental literature of adsorption dealing with the abnormal cases is now as extensive as that conforming to the simple theory. There are now numerous data showing abnormal variations in the extent of adsorption with both temperature and pressure, abnormal variations of the heats of adsorption with temperature and pressure, large variations in the velocity of attainment of equilibrium in different adsorption systems and in the velocity of evaporation of adsorbed gases inconsistent with present adsorption theory. Since these several factors in part determine the velocity of chemical processes at surfaces, the lack of a general theory covering such phenomena has resulted in an inadequate, and, in some cases, an incorrect treatment of the theory of chemical reactions at surfaces. It is the object of the present communication to point out the inadequacy of the classical theory of adsorption and

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[1] Benton, THIS JOURNAL, 45, 887, 900 (1923).

[2] Hückel, "Adsorption und Rapillarkondensation," Akademische Verlagsgesellschaft. 1928.

to indicate how it may very simply be modified to yield a general theory covering all types of adsorption.

It has been quite generally assumed on the basis of both theoretical considerations[3] and practical experience that the velocity of adsorption is great. There has been a constant tendency to ascribe any variation from a rapid process to the operation of secondary factors not essentially connected with the adsorption process. As one example, we may cite the assumption of diffusion processes, either in solutions or through the minute cavities or fissures in porous solid adsorbents, as responsible for the failure to establish equilibrium conditions rapidly in adsorption processes. Whatever importance may, in individual cases, be assigned to the operation of such secondary factors, it is the object of the present paper to propose and to establish by experimental evidence that the adsorption process per se is not necessarily a rapid process, may indeed be a very slow process, too slow to be measurable, and that for each adsorption process there is a characteristic velocity which is determined by the same factors which govern the velocity of chemical reactions, and therefore by temperature, pressure, concentration and the nature of the adsorbing surface. Since, as is now usual in discussions of chemical kinetics, we speak of the activation energy of a given chemical process we may, in the same sense, speak of the activation energy of an adsorption process. We shall show that, paralleling the enormous variation in activation energy of chemical reactions, there is a similar large variation in the activation energies of adsorption processes. Furthermore, we shall demonstrate that it is to this variability in activation energy of the adsorption process that the abnormalities we have already discussed are to be ascribed.

General Theory of Activation Energy in Adsorption Processes

The consequences of the concept of activation energy in adsorption processes may best be examined by a general consideration of the adsorption of a gas at a plane surface composed of a definite number of elementary spaces. The conditions governing adsorption equilibrium at such surfaces have already been detailed by Langmuir.[4]

(1) Equilibrium in Processes Involving Activation Energy.—Extending this treatment of equilibrium to processes involving activation energy, we shall consider the adsorption of a diatomic gas (X_2) which may be adsorbed on the surface (S) in question in two forms (a) as molecules, (b) as individual atoms. We may represent the two processes by means of the equations

$$\text{(a)} \quad S + X_2 \rightleftharpoons S(X_2)$$

$$\text{(b)} \quad S + X_2 \rightleftharpoons S\begin{pmatrix}-X\\-X\end{pmatrix}$$

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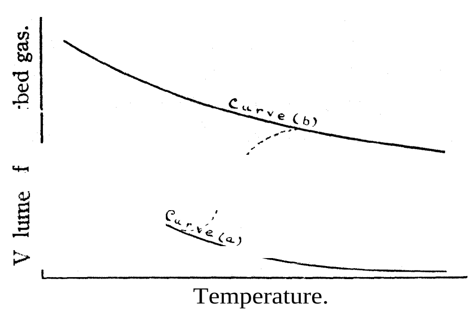
[3] **Lenard,** *Sitzb.* **Akad.** *Heidelberg, 5A, 16* **(1914).**

[4] **Langmuir, THIS JOURNAL, 38, 2221 (1916).**

We shall assume that, in a particular case, the heats of adsorption for the two processes (a) and (b) are respectively Q_a and Q, and that Q_b is greater than Q_a. We shall further assume that the activation energies are different and that the activation energy of process (a), E_a, is small, but that the activation energy of (b), E_b, is markedly higher. Under these conditions the activation energies of the reverse processes of vaporization are, respectively, E_a f Q_a and $E_b + Q_b$.

It is a consequence of the Langmuir concept of adsorption as due to the time lag between condensation and evaporation that the average time which molecules occupy the surface depends upon the ratio of the rates of adsorption and desorption and, therefore, accepting the above assumptions, on the ratio A, $e^{-E_a/RT}/B_a\ e^{-(Q_a + E_a)/RT} = (A_a/B_a)\ e^{+Q_a/RT}$ in the one case and on $(A_b/B_b)\ e^{+Q_b/RT}$ in the other case. Since the variations in A, and A_b, B_a and B_b are minor[5] as compared with the variation of the exponential for different values of Q_a and Q_b, it follows that the relative magnitudes of Q_a and Q_b largely determine the positions of the adsorption–temperature isobars for the two processes. For the case assumed, $Q_b > Q_a$, the isobar for (b) will lie above that for process (a) (Fig. 1). If the heats of adsorption for the two processes were equal the two curves would more nearly coincide. The differences would depend only on differences in A„ A_b, B_a and B_b. Were Q_b less than Q_a the curve for the isobar would lie below that of Q_a. There is no experimental evidence as yet of such a case.



Pig. 1.—Schematic representation of adsorption isobars with two activation energies for the adsorption processes.

(2) Extent **of Adsorption** and Temperature.—It may happen, by reason of the respective magnitudes of E_a and E_b, that, over a given range of low temperatures, the velocity of process (b) will be negligibly slow compared with that of (a). Under such circumstances the experimental results obtained will follow curve (a). As the temperature is raised there will be the normal decrease in adsorption of X_2 with temperature, but, simultaneously, there will be an increase in the velocity of process (b) so that, at sufficiently high temperatures, the experimental values obtained

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[5] In the simple Langmuir theory A_a and A_b are the rates at which molecules strike unit surface inelastically and are identical. The B factors in the evaporation process are similar to the factor C in the equation for a unimolecular reaction $dx/dt = C\,e^{-E/RT}$. Polanyi and Wigner [Z. *physik.* Cham., 139, 439 (1928)] have shown that, in this latter case, the variation of the C values in the available experimental data is very small.

will be due practically exclusively to the adsorption process (b). Between the two extremes of temperature there will be a region in which the results obtained will be intermediate between (a) and (b) and determined by the relative magnitudes of Q_a, Q_b, E_a and E_b. This intermediate stage may reveal itself by rising values of the adsorption at a given pressure with increasing temperature. This condition is indicated by the dotted line in Fig. 1. The location of the two adsorption curves with respect one to another will determine the magnitude of the increase in adsorption (if any) due to such causes.

(3) Adsorption Equilibrium and Nature of the Activation Process.—The conclusions thus reached with respect to the two adsorption processes involving, respectively, molecular and atomic adsorption are not limited to such processes but are applicable to any two processes of adsorption of a given molecular species producing any two forms of adsorbed product, the two processes differing in their activation energies. Dissociation of the molecule to yield atoms on the surface represents only one particular case of the general principle. It is apparent that adsorption may involve a plurality of types of change, in which case there will be a corresponding number of possible curves in Fig. 1 and a corresponding complexity in the observed adsorption–temperature relations. Thus, if a third type of adsorption occurred involving a higher activation energy E_c and a higher heat of adsorption Q_c, the isobar would lie above that of curve (b) and, in a given temperature range, there would be again a transition region of metastable adsorptions rising with increase of temperature. It should also be pointed out that if a case were found where Q_b was less than Q_a it is theoretically possible that the adsorption isobars experimentally realized would consist of two sections of decreasing adsorption with increasing temperature with an intermediate metastable region in which the decrease with temperature would be very much more pronounced. For simplicity, in the succeeding theoretical treatment only two types of adsorption will be discussed. It will be convenient to designate as type (a) the adsorption that occurs with low or negligible activation energies and as type (b) the adsorptions involving high activation energies. This in no sense, however, imposes on us the restriction that the adsorptions are of any particular type, for example, molecular and atomic. Any two adsorption processes of the same gaseous species may be involved.

(4) Activation Energy and Attainment of Equilibrium.—One further consequence of the present concept of activation energy on the results of experimental measurement may now be indicated. It is evident that because of the large activation energy, E_b, the portion of the curve (b) to the left of the dotted ascending curve cannot be experimentally realized by measurements conducted wholly at the lower temperatures involved. It is, however, also evident that values much higher than those correspond-

ing to curve (a) at the temperatures in question will be obtained if adsorption equilibrium is first established at higher temperatures, where both processes are occurring, and then the system be brought to the lower temperature. One can conclude from the theory that desorption of gas as far as curve (a) will not occur on cooling, that values considerably higher than those of curve (a) will be obtained and that these values will *approximate* to but will, in general, be somewhat lower than those for true equilibrium in the process (b) at the temperature in question.

(5) Effect of Varying Adsorbent.—Variation in the nature of the adsorbent with a given adsorbate will yield variations in the adsorption dependent on the values of Q_a, Q_b, E_a and E_b for the system in question. The discussion may be simplified if we assume that with every adsorbent the value of E_a is negligibly small. A variation in the value of E_b from case to case will involve a variation in the temperature at which the transition from adsorption along curve (a) to that along curve (b) occurs. For low values of E_b the transition will occur at low temperatures and may even result in the absence of all evidence of a transition. If E_b attains high values the transition will take place only at elevated temperatures. With a wide range of adsorbents these extremes of transition may be expected in practice.

(6) Effect of Concentration of Adsorbate.—The effect of increasing concentration of adsorbable gas may be indicated by again assuming that E_a is small and that the adsorption complex $S(X_2)$ is an intermediate stage in the formation of the second type of adsorption. The rate of the second stage will, therefore, be determined by the concentration of $S(X_2)$ and the activation energy E_b. The gas striking the surface will form initially complexes of type (a). Without the necessary activation energy, the molecules will re-evaporate. With increasing gas pressure the number of molecules striking the surface increases and, therefore, the probability of a collision with the necessary activation energy present at the place of collision will increase. The adsorption complex formed will become increasingly of the type (b). While this behavior will not be exhibited by the form of the adsorption isotherm it may be deduced from the values for the heat of adsorption (see below) at various equilibrium pressures.

(7) Effect of Non-Uniform Surface.—In actual practice adsorption studies are not made with uniform surfaces but with surfaces of varied activity. This reveals itself in the case of a single process of adsorption by a steadily falling value for the heat of adsorption. The adsorptions involving high heats of adsorption occur first and are succeeded by processes with lower and lower heat of adsorption. This factor introduces a constantly varying Q into the equations determining the evaporation process. Were the E factor constant, the effect of this falling Q would be to increase the rate of evaporation by increase in the term $e^{-(Q + E)/RT}$. There is

reason to believe, however, from analogy with the activation energy of chemical reactions at surfaces,[6] that the activation energy of adsorption processes should become larger and larger the less active the surface area. This increase in E with surface covered would tend, therefore, to offset to some extent the effect of diminishing Q.

In the case discussed in the preceding section where the extent of adsorption according to type (b) increases with increasing partial pressure of the gas, it is evident that the heat of adsorption–pressure (or amount of adsorbed gas) curve might show two descending sections corresponding mainly to types (a) and (b) with an intermediate section of transition values between. Such a possibility is shown diagrammatically in Fig. 2. It is also evident that, with suitable values for the activation energies and heats of adsorption, the preliminary fall in the first portion of the curve might be eliminated, leaving a curve showing a maximum. With low values for both E_a and E_b or, alternatively, at high temperatures, the curve would be entirely of the (b) type and show continuously falling values.

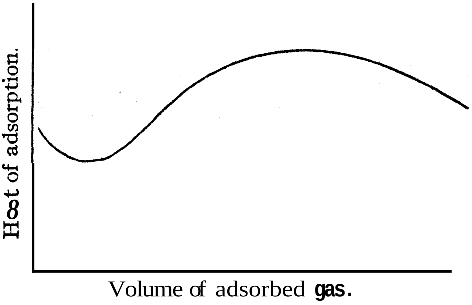

Fig. 2.—Variation of heat of adsorption with amount adsorbed for two adsorption processes having different activation energies.

(8) **Heat** of Adsorption **and** Temperature.—When, owing to a high value of E_b or the low temperature of operation, the adsorption is purely of type (a), the heats of adsorption measured will be characteristic of the adsorption process (a) and the extent of the surface covered. At high temperatures, where process (b) predominates, the heats of adsorption would in the same way be characteristic of that process. For this reason one can deduce a change in heats of adsorption with temperature. Since adsorption of the type (a) is the low temperature, non-specific, non-activated type, we can in general expect low heats of adsorption Q_a. For the specific adsorption involving activation and activation energy of adsorption, with the operation of valence forces at the surface, we should in general expect somewhat higher values for Q_b, of the order of magnitude familiar in chemical processes. It must be remembered, however, that since, for example, the activation process may involve in the case of a diatomic molecule a dissociation of the molecule into atoms, there is always the possibility of Q_b becoming a small magnitude.[7] At intermediate tempera-

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[6] Taylor, *Z. Elektrochem.*, 35, 542 (1929); "Treatise on Physical Chemistry," Vol. II, D. Van Nostrand Co., New York, 1931, 2d ed., Chap. XV, pp. 1081–1086.

[7] Compare, for example, the chemical reaction $N_2 + O_2 = 2NO$; the net heat of

tures where both adsorptions are involved, values intermediate to Q_a and Q_b would be obtained. It is also to be remembered in this connection, as already emphasized in the preceding section, that the Q value obtained under a given set of conditions is also a function of the nature of the surface covered, highest with the most active areas, whether the adsorption is of the (a) or (b) type.

(9) Extent of Saturation of a Non-Uniform Surface.—From the preceding discussion it will be evident that, on a non-uniform surface, it can readily follow that the combined operation of the Q and E values may result in a set of conditions such that only on a fraction of the surface may the activating adsorption (b) occur. If the temperature be such that adsorption of the type (a) is negligibly small, it would follow that the adsorption isotherms obtained would show all the characteristics of saturation with, however, only a small fraction of the surface covered with adsorbed gas. Such a condition would be of first importance in those chemical reactions at surfaces where activation was a condition precedent to reaction.

(10) The Temperature Coefficient of Surface Reactions and the Concept of Activation Energy of Adsorption.—It is well known that, in surface reactions, the observed activation energy of the chemical reaction is identical with the true activation energy only in exceptional circumstances (actually, in the so-called zero order reactions) For other reactions the observed and true activation energies are related to one another by equations which involve also the heats of adsorption of the reactants and products. Thus, as has been indicated[8] by Polanyi[9] and Hinshelwood,[10] for a unimolecular process involving decomposition of a substance A, the true energy of activation of the reaction (E_t) is related to the observed value E_0 by the equation

$$E_0 = E_t - Q_A \qquad (1)$$

where Q_A is the heat of adsorption of the substance A For a similar process involving retardation by a reaction product B the relation is

$$E_0 = E_t - Q_A + Q_B \qquad (2)$$

where Q_B is the heat of absorption of the reaction product B.

As pointed out by Hinshelwood, these equations presuppose that the establishment of adsorption equilibrium is rapid in comparison with any disturbance of it due to the removal of the molecule in chemical change. When, however, owing to the operation of an activation energy term, E, the rate of adsorption leading to activation is very materially decreased, this

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this reaction is **−43** kg. calories, as it involves the heat of dissociation of nitrogen and oxygen molecules, respectively, 200 and 120 kg. calories.

[8] For a general treatment of this subject see Taylor, "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, 1931, Vol. II, Chap. XV, p. 1081.

[9] Polanyi, *Z. Elektrochem.*, 27, 143 (1921).

[10] Hinshelwood, "Kinetics of Chemical Change," 2d ed., Oxford University Press, Oxford, 1929, Chap. VIII, p. 232.

condition may no longer hold and the equations derived will be inapplicable. This consideration applies to both Equations 1 and 2 above.

(11) Velocity of Evaporation and Adsorption of Molecules.—It has been customary hitherto in treating the velocity of evaporation of adsorbed molecules to assume its proportionality to $e^{-Q/RT}$ where Q was the heat of adsorption. This is only true so long as the activation energy of the adsorption process is negligibly small. The correct expression for the evaporation process involves $e^{-(E+Q)/RT}$; it is evident that cases might arise in which great differences in the velocity of evaporation of two adsorbed gases were obtained, even though the Q's were identical, because the E's were markedly different. It is also not impossible that, owing to marked differences in the values of E in two cases, the velocity of evaporation in the process with a higher Q value should be more rapid than the velocity of evaporation with the lower Q. In the reverse process of adsorption the same principles apply.

With this review of the general principles involved in the application of the concept of activation energy to adsorption processes accomplished, we may now pass to an examination of experimental data in order to ascertain how far the general conclusions reached in the preceding may find experimental verification. We shall examine data with reference to adsorption processes for such gases as hydrogen, oxygen, carbon monoxide, nitrogen, sulfur dioxide and water vapor on a variety of surfaces. We shall find our theoretical conclusions abundantly verified by practical experience.

Experimental Data and the Concept of Activation Energy of Adsorption

It will be convenient to classify the experimental data with reference to the gas adsorbed, discussing in each case the various adsorbents studied.

Adsorption of Hydrogen.—There are pertinent data for hydrogen adsorption on the catalytically active metals, nickel, copper, platinum, palladium, as well as on charcoal and a few oxide surfaces.

NICKEL.—The most abundant data are available in this case on nickel surfaces. The recent research of Benton and White,[11] extending the earlier studies of Gauger and Taylor,[12] provide data for adsorption equilibria over the temperature range —209 to 305°. Benton and White's results show that the activation energies involved are low since the transition (Section (2) of General Theory) from a region of low adsorption to one of high adsorption occurs in the temperature range of —190 to —100°. Above this latter temperature, the activation process is rapid. Benton and White observed different amounts of adsorption at low temperatures according as one operated exclusively at low temperatures or saturated at high temperatures and then cooled down. This checks with the conclu-

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[11] Benton and White, THIS JOURNAL, 52, 2325 (1930)

[12] Gauger and Taylor, *ibid.*, 45,920 (1923).

sions of Section (4) in the General Theory. The increased adsorption obtained by cooling to −191° over that observed at 0° will be in part due to increased adsorption of the activated adsorbate in passing through the metastable region plus any additional hydrogen adsorbed with the low activation energy.

Benton and White's data on the velocity with which equilibrium is attained also conform to the requirements of the present theory. At the temperatures of −183 and −191°, "the pressure became constant almost immediately after admitting the gas;" at these temperatures we have type (a) adsorption with low values of E_a. In the higher[13] temperature range equilibrium was fairly rapidly established at very low pressures, slowly at moderate pressures and somewhat less slowly at higher pressures. These are consistent with an adsorption involving an activation energy as set forth earlier in Sections (6) and (11). Gauger and Taylor had earlier noted that an interval of ten minutes was insufficient at room temperatures and upward to establish equilibrium and that isotherms thus obtained were different from those obtained by de-sorbing gas from the surface. The work of Gauger and Taylor also showed the effect discussed in Section (9) of the varying extent of surface covered, with apparent saturation, at different temperatures.

An increase in the heat of adsorption with increase of surface covered has been shown in Section (8) to be a possible consequence of adsorption processes involving activation energy. Such an increase was demonstrated by Fryling[14] in the case of active nickel catalysts. In other cases with less active adsorbents this phenomenon was absent in the measurements at 0°. In all cases at this temperature the heats of adsorption were high (*ca.* 15,000 cal.) as compared with those involving only van der Waals forces.

One can summarize, therefore, the case of nickel–hydrogen by observing that it conforms closely to the conditions imposed by the general theory. In the system metal–hydrogen this constitutes the best investigated case. With other metals the data are scantier and, to economize space, they will only be recorded in bare outline.

PLATINUM.—Platinum shows the phenomenon of *diminishing* adsorption with decreasing temperature as noted with nickel above.[15] Apparently, the decreased absorption sets in at a higher temperature than in the case of nickel since de Hemptinne records diminished adsorption at −78°, whereas the decrease with nickel occurred below −110°. G. B. Taylor, Kistiakowsky and Perry[16] record high heats of adsorption at 0° of the order of 10,-

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[13] We cannot explain why the equilibrium below −191° was slowly established unless it was due to the experimental difficulty of maintaining constant temperature.

[14] Fryling, *J. Phys. Chem.*, *29*, 1235 (1925).

[15] De Hemptinne, *Z. physik. Chem.*, 27, 429 (1898).

[16] G. B. Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, *34*, 799 (1930).

000–30,000 calories. A determination of the heat of adsorption in the low temperature range would be revealing. On the present thesis it should be much lower than the values at 0°.

PALLADIUM.—De Hemptinne records a higher absorption of hydrogen by palladium at −78° than at 0°. On the other hand, there is excellent experimental evidence by Firth[17] that massive palladium foil will not take up hydrogen at liquid-air temperatures. Palladium saturated with hydrogen at ordinary temperatures did not evolve this gas on cooling to liquid-air temperatures. In a later communication, Firth[18] compares the absorption of palladium black samples which have been either (a) saturated at 110° with hydrogen and then cooled in hydrogen to the temperature of measurement or (b) have been saturated with hydrogen only at the temperature in question. In both cases there is a decrease in absorption with increase of temperature from liquid-air temperatures upward. Prior saturation at 110° always gave the higher values. The curve (b) shows a pronounced minimum around 20°, which indicates that an activation sets in around this temperature, leading to the increased adsorption represented by the difference in values of curves (a) and (b). A similar minimum sorption has also been found by Gutbier, Gebhardt and Ottenstein.[19] In the case of palladium conditions are complicated by the high solubility of the gas in the metal. This point will be treated subsequently in a special paragraph. There appear to be no data on heats of adsorption.

COPPER.—There is no evidence in the published data of adsorptions on copper similar to that cited in the preceding cases. Through the courtesy of Dr. R. N. Pease, however, some unpublished data by C. A. Harris may be quoted to the same effect.[20] On a particular sample of active copper, Harris found a pronounced maximum in the adsorption of hydrogen on copper between 0 and 100°. At 56.5° and 760 mm. pressure the adsorption was 35% greater than at 0°. At 100 and 155° the adsorption was slightly greater than at 0° but less again at 193° There is also good evidence in this work that by saturating at higher temperatures and then returning to 0° the adsorptions recorded could be increased many-fold (cf. Section (4)). These latter results should be accepted with reserve since the adsorbed hydrogen was not recovered from the surface after the experiment. There is, however, every reason to believe that such results are quite sound and in accord with those already recorded That such is the case is emphasized by the knowledge that Taylor and Kistiakowsky[21] found a pronounced

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[17] Firth, *J. Chem. Soc.*, 117,171 (1920).

[18] Firth, *ibid.*, 119, 1120 (1921).

[19] Gutbier, Gebhardt and Ottenstein, *Ber.*, 46, 1453 (1913).

[20] Master's Thesis, University of Virginia, 1924.

[21] Taylor and Kistiakowsky, *Z. physik. Chem.*, 125,341 (1927)

maximum in the curve for the heat of adsorption of hydrogen on an active copper catalyst. Some unpublished data by Washburn also indicate an activation energy for the hydrogen adsorption. Although the heat of adsorption is only 10,000 calories as compared with 15,000 calories for ethylene, it is a familiar experimental fact that it is easier to remove this adsorbed ethylene from the surface than it is to remove hydrogen (cf. the discussion of carbon monoxide on platinum later).

The evidence cited in this case would indicate that the activation energy necessary in the case of the copper–hydrogen system is markedly higher than with nickel, platinum and palladium.

CARBON.—There is indirect evidence that, with carbon, activation occurs at even lower temperatures than with nickel and palladium. At $-78°$ and at liquid air temperatures[22] the adsorption of hydrogen on charcoal is very much greater than at 0°, and greatest at the lowest temperature. Above $-200°$, therefore, there is no evidence of diminishing adsorption. There is, however, indirect evidence that even at liquid hydrogen temperatures adsorbed hydrogen is at any rate in part activated. Bonhoeffer and Harteck[23] showed that charcoal is an excellent catalyst for the conversion of ortho- to para-hydrogen at these low temperatures. There is good reason to believe that this interconversion of the two forms must occur through the atomic state, which, therefore, must be present at the surface.[24] If so, the activation energy of the adsorption process must indeed be small. It is pertinent to point out that the data presented above for nickel, platinum and palladium provide the reason for the inefficiency of these metals in the para-hydrogen conversion at liquid-air temperatures and lower, whereas they are good catalysts for the reconversion process at room temperatures. This peculiar behavior puzzled both Bonhoeffer and Harteck, who believed, however, that it might be due to some "triviale Ursache." Measurements of the heats of adsorption over a range of temperatures and pressures would be instructive in respect to the matters here raised.

OXIDE CATALYSTS.—It is known that series of oxides are efficient agents for hydrogenation–dehydrogenation processes and that these operate normally in a higher temperature range than the metal hydrogenation catalysts. On this basis one might anticipate that the phenomena discussed concerning adsorption by the metals in the low temperature range might be repeated with the oxide catalysts in a higher temperature range. Evidence is accumulating that this is true.

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[22] Dewar, *Proc. Roy. Inst.*, 18, **437** (1906).

[23] Bonhoeffer and Harteck, *Z. physik. Chem.*, 4B, **113** (1929)

[24] The conversion of ortho- to para-hydrogen involves a change of the nuclear spin of one hydrogen atom. According to present accepted ideas this can only occur by a definite exchange of atoms. Cf. Farkas, Z. *Elektrochem.*, 36,782 (1930).

Garner and Kingman have recently reported[25] that hydrogen (or carbon monoxide) adsorbed at low pressures and room temperature on ZnO–Cr_2O_3 catalysts was given off at 100–120°, but after twenty to thirty minutes was readsorbed on the surface of the catalysts. This is precisely what is expected from *a* high temperature adsorption with high activation energy. Indeed, this concept of activation energy requires the evaporation and re-absorption as two independent processes, a phenomenon which appeared to Garner and Kingman as "curious." It is in accord with the experience of Taylor and Kistiakowsky[26] with zinc oxide and with zinc–chromium oxide catalysts which showed that desorption only occurs rapidly by evacuation above 300°. Further, on zinc–chromium oxides, Kistiakowsky and Flosdorf[27] have recently shown the presence of a maximum in the heat of adsorption–pressure curve as with hydrogen on nickel and copper. Garner and Kingman state that the phenomenon they observed with zinc oxide is given by copper oxide.

With hydrogen on manganous oxide some measurements by Williamson at present in progress in this Laboratory have shown a pronounced increase of hydrogen adsorption with temperature. At 0 and 100° negligible amounts of hydrogen are adsorbed. At 184° adsorption can just be demonstrated while at 305° as much as 10 cc. of gas has been adsorbed by the sample in question. Our work shows also that on saturating at the higher temperature and cooling to lower temperatures, complete desorption does not occur. These experiments, therefore, extend the region of transition from one type of adsorption to another, from temperatures below $-110°$ in the case of metals to above 200° in the case of oxides.

Dr. H. N. Alyea has directed my attention to the experiments of Bone and Wheeler[28] with quartz at 650° in which it was found that considerable quantities of hydrogen were taken up at this temperature. In view of the preceding examples a renewed investigation with glass and quartz in this region is desirable and is being undertaken by Dr. Alyea. One might observe that it seems doubtful that under the circumstances given the adsorption should be of atomic hydrogen since Langmuir has shown that glass surfaces loaded with atomic hydrogen at liquid-air temperatures readily yield this hydrogen in the molecular form on raising the temperature. The possibility of occlusion or solution of the gas in the preceding cases will receive separate discussion at a later stage.

Adsorption of Oxygen.—The data on oxygen adsorption which are of interest in respect to activation energy concern such varied surfaces as carbon, silver, gold, nickel, tungsten and platinum.

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[25] Garner and Kingman, *Nature*, **126**, 352 (1930).

[26] Taylor and Kistiakowsky, THIS JOURNAL, **49**, 2468 (1927).

[27] Kistiakowsky and Flosdorf, *J. Phys. Chem.*, *34*, 1907 (1930).

[28] Bone and Wheeler, *Phil. Trans. Roy. Soc.*, **206A**, 1 (1906).

CARBON.—It has long been recognized that the adsorption of oxygen on carbon did not obey the simple general theory of adsorption at solid surfaces but no satisfactory treatment of the subject has hitherto been available. It may now be shown that the adsorption consists of more than one type and that activation energy is involved. There does not appear to be any evidence of an increase of adsorption with increase of temperature. There is definite evidence, however, of two types of adsorption similar to those discussed in the general theoretical portion of this paper. Dewar[29] showed that the oxygen adsorbed by charcoal at −185° was given off on heating to room temperature. Lowry and Hulett showed[30] with a given char that of the oxygen which saturated the sample at room temperatures, not more than 50% was recoverable as oxygen on evacuation. The residue could only be recovered as carbon oxides. The extent of oxygen fixation was a function of the char. Rhead and Wheeler showed that the oxygen retained by charcoal[31] at temperatures of 200° and upward could not be recovered as oxygen at all, only as carbon oxides. The influence of temperature on the fixation or activation process is evident not only from these several researches but also from the experimental data of Rhead and Wheeler in the temperature range of 300–600°.

The data for heats of adsorption on charcoal are also illuminating. At −185° Dewar obtained a value of 3744 calories per mole. At higher temperatures the principal data have been obtained by Garner and his coworker and by Keyes and Marshall.[33] The data of the latter showed a heat of adsorption at 0° of 72,000 calories per mole. More recently Marshall and Bramston-Cook show values falling from 89,600 calories at nearly zero concentration to 70,000 calories, at which value it flattens prior to the normal fall. The data of Garner and his colleagues all agree in indicating very low values on the earlier portions of the curve with values rising subsequently to a maximum and then a falling curve, as in the experiments with hydrogen on nickel, copper and zinc–chromium oxides. Whatever the ultimate explanation of these experimental discrepancies may be,[34] is immaterial to the present discussion. It is sufficient to

[29] Dewar, *Proc. Roy. Soc.* (London), 74, 126 (1904); *Proc. Roy. Inst.*, 18, 184 (1905).

[30] Lowry and Hulett, THIS JOURNAL, 42, 1408 (1920).

[31] Rhead and Wheeler, *J. Chem. Soc.*, 101, 831 (1912); 103, 461 (1913).

[32] Blench and Garner, *J. Chem. Soc.*, 125, 1288 (1924); Garner and McKie, *ibid.*, 2451 (1927); McKie, *ibid.*, 2870 (1928); Cameron, *Trans. Faraday Soc.*, 26, 239 (1930).

[33] Keyes and Marshall, THIS JOURNAL, 49, 156 (1927); Marshall and Bramston-Cook, *ibid.*, 51, 2019 (1929).

[34] See Bull and Garner, *Nature*, 124, 409 (1929). The simplest explanation would seem to be that the divergencies were due to the difference in methods employed. The ice calorimeter permits longer time intervals for the measurement during which time the activation process may have occurred, the high heat value being thereby obtained. The Garner method operates on shorter time intervals and so adsorption without activation is probably the major process whose heat effect was measured.

record the existence of rising heats of adsorption in yet another case of abnormal adsorption of a gas at a solid surface. On extending their measurements to high temperatures, Blench and Garner obtained heats of adsorption as high as 227,000 calories. The extraordinary increase in the heat data from liquid-air temperatures to high temperatures is striking evidence of a plurality of processes in the fixation of oxygen by charcoal.

SILVER.—Adsorption experiments by Benton and Elgin, with oxygen on silver,[35] are in excellent agreement with the concept of activation energy. Their measurements indicate an increasing adsorption in the region 26–110° and a great slowness in attaining equilibrium. At 110° a period of twenty-four hours was required before a constant value of 14.84 cc. adsorption was attained. The adsorption was rapid in the first stages but after the addition of each successive quantity a gradual and long-continued pressure decrease occurred. Furthermore, only a very small fraction of the total amount adsorbed could be recovered by evacuation. It would be interesting to extend such measurements to very low temperatures to see how low in temperature this irreversibility extends. A measurement of heats of adsorption over the same temperature range should also be instructive. In this same investigation the authors record an immeasurably small adsorption of hydrogen at 26 and 110°. Measurements with this gas above and below this temperature range would be instructive, especially since silver is known to possess a certain small activity as a hydrogenation–dehydrogenation catalyst.

GOLD.—Experiments by the same authors, with oxygen on gold,[36] are compelling evidence in support of adsorption with an activation energy. The authors find that "at about 650 mm. pressure the gold took up 3.57 cc. at 98°, 4.78 cc. at 130° and 5.73 cc. at 157°." Measurements were continued at a temperature of 130° for forty-eight hours after apparent equilibrium had been reached without altering the above value. Without removing the oxygen the temperature was raised to 157° and the system allowed to come to equilibrium, which also was the same as before. The temperature was then lowered to 130°. Although this temperature was maintained for eighty hours, no decrease occurred in the amount of gas adsorbed. This is convincing proof that it is the activation energy of the process which is determining the extent of adsorption at any temperature. Benton and Elgin observe that at 130° approximately twenty-four hours are required for attainment of apparent equilibrium, one hundred eight hours at 98°.[37] At 25° an adsorption of only 0.1 cc. had occurred in seven

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[35] Benton and Elgin, THIS JOURNAL, 48, 3027 (1926). This and the example next discussed were called to my attention by my colleague, Dr. J. C. Elgin.

[36] Benton and Elgin, *ibid.*, 49, 2426 (1927).

[37] If one uses these times as a rough measure of reaction velocity at the two temperatures one obtains by insertion in the equation d ln $k/\mathrm{d}t = E/RT^2$ the value of $E =$

hours of contact. They further demonstrate that the rate of adsorption is nearly independent of the gas pressure, which indicates that the activation energy is supplied to adsorbed gas and hence by the surface. The rates of adsorption with gold were pronouncedly slower than with silver. The oxygen adsorbed at 130° was not recoverable by evacuation. Experiments at very low and at higher temperatures would be of great interest both with respect to adsorption, reversibility and heat of adsorption. On the gold sample, a scarcely measurable adsorption of hydrogen occurred at 130°. The study of higher temperatures should be of interest.

NICKEL.—A similar condition apparently holds with an active nickel surface but at somewhat lower temperatures. Russell[38] has recently found that oxygen is strongly, irreversibly and rapidly adsorbed by nickel in an ice-bath. The heat evolution is of the order of 100,000 calories per mole adsorbed.

Experiments with oxygen and nickel at liquid air temperatures are to be undertaken by Dr. Russell at the writer's request.

TUNGSTEN.—The retention of oxygen by clean tungsten filaments was demonstrated by Langmuir, who also showed that the stability of the oxide film was so great that no interaction with hydrogen occurred up to 1500°K. The film may be formed at room temperatures but its properties are somewhat different from that produced by heating the filament in oxygen at low partial pressures at about 1900°K. for a few seconds.[39] From its behavior toward cesium under these conditions there is reason to believe that the oxygen taken up at 1900°K. is then probably held as negative oxygen ions. The heat of adsorption of this oxygen has been estimated by Langmuir to be 160,000 calories per gram atom.[40] Dr. S. Dushman has kindly consented to ascertain whether this strong affinity between tungsten and oxygen manifests itself at liquid-air temperatures. Langmuir believes that oxygen may be adsorbed on tungsten surfaces in at least three different forms.

PLATINUM.—Langmuir similarly showed that oxygen was held tenaciously by platinum and could be removed by reaction with hydrogen. Recent experiments[41] have shown that the heat of adsorption may be as high as 163,000 calories per mole of oxygen adsorbed and that values in the neighborhood of 100,000 are usual. The adsorption process is fairly rapid

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13,830 calories. To this value must be added the activation energy of the molecular absorption process since this influences the concentration of molecules at the surface at the two temperatures. The data, therefore, suggest in this case an activation energy of around 15,000 calories.

[38] Personal communication by Dr. W. W. Russell of Brown University, Providence, Rhode Island.

[39] Langmuir and Kingdon, *Phys.* Rev., 24, 570 (1924).

[40] Langmuir, Lecture at Princeton University, September, 1929.

[41] G. B. Taylor, Kistiakowsky and Perry, J. Phys. *Chem.*, 34, 799 (1930).

at 0° but detailed experiments at lower temperatures have not yet been performed. Langmuir states[42] that in some earlier work he observed that platinum at liquid-air temperatures took up a certain amount of oxygen. On warming the system some oxygen was evolved, but at higher temperatures this same oxygen was once more reabsorbed. This exper'imental fact indicates a change in the state of oxygen absorption between liquid air and room temperatures.

Adsorption of Carbon Monoxide.—Experimental evidence in support of the concept of activation energy of adsorption processes is available also in the adsorption of carbon monoxide by nickel, copper, platinum and palladium.

NICKEL.—Carbon monoxide in contact with nickel shows strikingly the function of temperature in the adsorption process. At ordinary temperatures, as is well known, carbon monoxide and nickel react to form nickel carbonyl. At 180° this reaction is suppressed and a truly reversible adsorption of carbon monoxide occurs.[43] At about 270° the carbon monoxide begins to be irreversibly adsorbed and a portion remains in contact with the surface on evacuation. It is this carbon monoxide which reacts with hydrogen to yield methane and water, or with other carbon monoxide gas to yield carbon dioxide and carbon. We might suggest that at this temperature the atoms of carbon monoxide are now attached to the nickel surface directly as Ni_3C and NiO. Indeed experimental evidence indicates the presence of nickel carbide as an intermediate stage in methane synthesis.[44] It is this last process, whatever its nature, that involves the high activation energy. Further, it can be demonstrated that this process of activation only occurs at 270° on the most active portions of the nickel surface since relatively small amounts of sulfur compounds poison the surface for the methane reaction. In this case, therefore, we have an experimental example of the case discussed in Section (9) of the general theory in which only a small fraction of the total surface is capable of effecting the activation in question.

COPPER.—On copper surfaces carbon monoxide showed a curve for heat of adsorption as a function of surface covered which first fell, then rose to a maximum and then once more showed falling values.[21] This is the case discussed in Section (7) of the general theory and illustrated in Fig. 2. It constitutes good evidence of a dual nature of the adsorption process on copper. The heats of adsorption measured were of the order of 10,000–20,000 calories. No evidence as to rising adsorptions over a temperature range has been located in the literature but a study of the region below 0° would be of interest. It is known that no such activation of the carbon

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[42] Personal communication.

[43] Taylor and Burns, THIS JOURNAL, 43, 1283 (1921).

[44] Bahr and Bahr, Ber., 61B, 2177,2465 (1928).

monoxide molecule occurs on copper as takes place on nickel at 300°. Even up to higher temperatures no decomposition of carbon monoxide to carbon dioxide and carbon occurs on copper nor can methane be produced under ordinary conditions with copper. One may thus conclude that the activation energy of this latter adsorption on copper is very high indeed.

PLATINUM.—De Hemptinne records a less adsorption of carbon monoxide on platinum at −78° than at +15°. Taylor and Burns found smaller values at 25° than at 110°. It is well known that the reversibility of carbon monoxide adsorption on platinum is slight.[45] G. B. Taylor, Kistiakowsky and Perry obtained measured values of the heat of adsorption with as much as 21.7 cc. of adsorbed gas with heats of adsorption greater than 20,000 calories per mole. Of this only 0.7 cc. was removed by degassing at 350°. The significance of this is apparent when we find that on the same catalyst 5 cc. of hydrogen with heats of adsorption greater than 20,000 calories can be removed by degassing at 250° for four hours. Such results obviously suggested to the authors that "the true rate of evaporation from the surface must be influenced by other factors besides the heat of adsorption to a very considerable degree." The authors showed that differences in the rates of diffusion are too small to account for the observed phenomena, this being the reverse of the observation by Benton and Elgin cited above concerning oxygen on gold, namely, that the gas pressure was without influence on the rate of adsorption. It follows that in the case of carbon monoxide adsorption on platinum the activation energy of the adsorption process must be higher than that of hydrogen.

PALLADIUM.—De Hemptinne found an increase in carbon monoxide adsorption between −78 and +15°. Taylor and Burns found no change between 25 and 110°.

OXIDE CATALYSTS.—We have already referred to the observation of Garner and Kingman that carbon monoxide adsorbed on $ZnO-Cr_2O_3$ surfaces at room temperature was first evolved on heating to 110° and then readsorbed after twenty to thirty minutes. This is direct evidence of adsorption having an activation energy. The same conclusion is abundantly evident from the comprehensive paper by Benton[1] on the adsorption of gases by oxide catalysts. His data on the extent of "primary" and "secondary" adsorptions of carbon monoxide, their variation with temperature and pressure are all excellent material for a demonstration that the so-called "primary" adsorption is a process involving a high activation energy compared with that of the "secondary" adsorption. Indeed one might inquire how, without this concept of activation energy, one is to account for the fact that "secondary" adsorption, involving the weaker forces of adsorption, occurs at −78° in preference to "primary" adsorption which only becomes important at higher temperatures but in which the

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[45] Langmuir, THIS JOURNAL, 40, 1361 (1918).

forces of adsorption are stronger. It is evident that secondary and primary adsorptions are in reality processes with low and with larger activation energies. None of Benton's data show an intermediate temperature range of increasing adsorption, a factor which is evidently to be attributed to the relative positions of curves (a) and (b) of Fig. 1 in these cases. Benton observes, however, that the carbon monoxide could be much more easily removed after a measurement at $-79°$ than at $0°$.

Adsorption of Nitrogen.—Adsorption of nitrogen with activation is of obvious importance in ammonia synthesis. The recent work of Frankenburger and Mayrhofer on iron surfaces laid down by condensation of iron vapor[46] along with ice or sodium chloride molecules on glass was successful in demonstrating a stoichiometric ratio $Fe:H_2$ of 1:1 for hydrogen adsorption. No similar adsorption of nitrogen could be detected although there were slight indications of a nitrogen adsorption if hydrogen was also present. This suggested to the authors that thermal activation of the nitrogen is also necessary. That such activation leads to nitrogen fixation on the iron surface at least in the presence of hydrogen is evident from the fact that in the dissociation of ammonia streaming over heated iron relatively large amounts of nitrogen are continuously present on the surface. It follows then, from the principle of "microscopic reversibility" or "entire equilibrium," that a nitrogen–hydrogen mixture passed over iron will lead to a fixation of nitrogen on the surface. In this case also, therefore, we are led to postulate activation energy of the adsorption process.

Adsorption of Water Vapor.—From what has preceded it is evident that we may expect dual processes of adsorption of water vapor on such surfaces as are active in hydration and dehydration processes, and hence on such surfaces as alumina, thoria and the like. This does not seem to have been directly tested. There is, however, one very instructive if indefinite piece of evidence that such dual activation occurs. Dohse and Kälberer[47] found that the decomposition of isopropyl alcohol on bauxite was a unimolecular reaction, inhibited by the product water and having an apparent activation energy of 39,000 calories. The true activation energy of the process, obtained from a study of the zero order reaction by constant removal of the water vapor or by investigation at low surface concentrations, gave a value of 26,000 calories. For a unimolecular process inhibited by a product, water, we saw in Section (10) of the general theory that the Polanyi–Hinshelwood equation gives

$$E_{\text{obs.}} = E_{\text{true}} - \lambda_{C_3H_7OH} + \lambda_{H_2O}$$

For low surface concentrations Dohse and Kalberer actually measured the heats of adsorption, finding $\lambda_{C_3H_7OH}$ to be 21,000 calories and $\lambda_{H_2O} = 13,000$ calories. From the equation, then, we have

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[46] Frankenburger and Mayrhofer, *Z. Elektrochem.*, 35, 590 (1929).

[47] Dohse and Kälberer, *Z. physik. Chem.*, 5B, 131 (1929).

$$E_{\text{true}} = 39{,}000 + 21{,}000 - 13{,}000 = 47{,}000 \text{ calories}$$

in obvious disagreement with the value of 26,000 calories found for the uninhibited zero order reaction. This discrepancy is even more conspicuous when we note that water vapor with a measured heat of adsorption of 13,000 calories is inhibiting the decomposition of isopropyl alcohol with a measured adsorption heat of 21,000 calories. This shows that the heat of adsorption is no simple measure of the rate of evaporation, an additional example, therefore, of the point raised in Section (11) of the general theory and in the case of platinum–carbon monoxide adsorption. To account satisfactorily for inhibition by water in the present case we are forced to assume an activation energy of the order of at least 22,000 calories greater than that of isopropyl alcohol. Such a divergence would bring both types of experimental result into agreement.[48]

Adsorption of Sulfur **Dioxide.**—PLATINUM.—The data already cited with respect to reversibility in the adsorption of hydrogen and carbon monoxide on platinum may be supplemented by the case of sulfur dioxide. G. B. Taylor, Kistiakowsky and Perry showed that of 6.5 cc. of gas held with heats larger than 20,000 calories only 3.5 cc. is removed by degassing at 350°, whereas more than 5 cc. of hydrogen with heats greater than 20,000 calories could be removed at 250°. On another sample of platinum, sulfur dioxide with heats smaller than 20,000 calories could not be removed at 250° whereas, with hydrogen of higher heats of adsorption, removal was readily accomplished. It is thus necessary to postulate a high heat of activation for the adsorption of sulfur dioxide on platinum.

General Conclusions

It has been suggested that the slow process, requiring an activation energy, might be a solution process in the material and that the slowness of diffusion to the interior of the adsorbent was the rate-determining factor. The presence of palladium, in the list of examples cited, at once suggests this possibility. It ought to be emphasized, however, that this cannot be the general explanation. In many of the cases here dealt with the quantities of gas involved are of several orders higher magnitude than the known solubility of the gas in the substance concerned. The surface factor, too, is paramount in the cases we have been considering, whereas this factor is not of such importance where solubility is concerned. The variation of adsorption with pressure is not that to be expected on the basis of solubility.

It is obvious that the concept of activation energy for adsorption processes here developed is of great importance in the general problem of reactivity at surfaces. It is evident at once that adsorption per se need

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[48] There is the additional possibility that, at the reaction temperature, the heat of adsorption of water is markedly greater than that recorded above. This would require a smaller spread between the activation energies.

not be related to catalytic activity. There should be, however, a closer concordance between reactivity and the adsorption processes occurring with marked activation energy. Limitations of space prevent such a discussion in this place but opportunity to treat this problem separately will be taken at a later date.

Summary

A general theory of adsorption involving several forms of adsorption at surfaces has been shown to lead to a number of conclusions capable of experimental verification. It has been shown, from abundant data in the literature, that these conclusions are already experimentally verified. It seems necessary, therefore, to abandon entirely the assumption implicit in older theories that the processes of adsorption are rapid. The assumption that all processes of adsorption possess their own characteristic activation energies permits a single general treatment of adsorption inclusive of processes which hitherto have been considered separate and unrelated. It has been shown that the only essential distinction between "secondary" and "primary" adsorptions or between "reversible" and "irreversible" adsorptions is that "secondary" or reversible adsorption processes are adsorptions normally with small heats of adsorption and small activation energies and that in the so-called "primary" or "irreversible" adsorptions, moderate or large energies of activation are involved, frequently with high heats of adsorption. The velocities of these latter processes may indeed be extremely slow. In general, it is the adsorptions with the higher energies of activation which are important in catalytic change.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY (NO. 648) AND OF VASSAR COLLEGE]

THE QUINHYDRONE ELECTRODE. II

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RECEIVED DECEMBER 16, 1930 PUBLISHED FEBRUARY 9, 1931

Introduction

While there have been a number of papers which included work more or less directly related to the effect of oxygen on the potential and to the use of nitrogen in the preparation of the quinhydrone half cell, we are not aware of any study having been made of the reproducibility of the electrode possible under conditions of preparation and use which excluded oxygen in acid solution. It is the object of this paper, then, to present the results of such a study made in 0.1 N hydrochloric acid and to compare the reproducibility of the quinhydrone electrodes prepared with nitrogen with those obtained with air and upon which we have previously reported.[1]

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[1] Morgan, Lammert and Campbell, THIS JOURNAL, 53, 454 (1931).

Preparation and Purification of Materials.—The materials used have been described in the first paper of this series with the exception of the following.

Nitrogen.—Tank nitrogen from the Air Reduction Sales Company was reduced to the desired pressure and passed successively through solutions of alkaline permanganate, alkaline pyrogallic acid, distilled water, and the electrolyte used in the cell before it was conducted to the cell.

Oxygen.—Tank oxygen supplied by the Linde Air Products Company was purified by the same method as the compressed air.

Apparatus.—The electromotive force measurements were made with the apparatus and with the precision described in the first paper, to which reference has been made; the gases were conducted through the purifying solutions, kept at the same temperature, before being conducted to the cell solution containing the quinhydrone.

The electrodes and electrode vessels were identical with those used for the experiments in air except that in the stopper of the electrode vessel a gas inlet tube replaced the stirrer.

Procedure and Results.—The procedure adopted for the determination of the reproducibility of the quinhydrone electrode under circumstances which permit the use of nitrogen was in every respect identical with the procedure adopted in the first paper of this series[1] except that the electrodes were dried with nitrogen instead of with air and the solutions stirred with nitrogen instead of by a mechanical stirrer. The procedure was carried out in such a way that no air was admitted to the electrodes after they were immersed in alcohol. Nitrogen was bubbled through the alcohol for several minutes, the alcohol was forced out of the electrode vessel with nitrogen, and the flow of nitrogen was continued while the quinhydrone solution was being poured into the electrode vessel as well as during the time the electrodes were in the thermostat. Later results obtained when the electrodes were dried in air as described in the first paper and then stirred with nitrogen indicated that the more elaborate procedure of drying with nitrogen was unnecessary; these results will be discussed presently. In some cases oxygen or compressed air was substituted for nitrogen in both drying and stirring operations, the procedure being similar.

The results obtained with nitrogen-dried electrodes and nitrogen-stirred solutions are collected in Table I. The averages and deviations were calculated by the method used for the potentials measured in air, which results were presented in Table I of the first paper of this series.

In Table II are given the percentages of the total number of cells measured in nitrogen which lie within certain ranges.

A number of conclusions are obvious from the results collected in these tables. In the first place, quinhydrone electrodes prepared with nitrogen are far more reproducible than those prepared with air. The average

TABLE I

COMPARISON OF THE REPRODUCIBILITY OF THE POTENTIAL DIFFERENCES OBTAINED AFTER SIXTY MINUTES IN 0.1000 *N* HYDROCHLORIC ACID SOLUTION SATURATED WITH QUINHYDRONE BETWEEN ELECTRODES MADE OF METALS OF DIFFERENT DIMENSIONS AND COMPOSITIONS WITH DIFFERENT PRE-TREATMENTS; ELECTRODES DRIED AND SOLUTIONS STIRRED WITH NITROGEN[a]

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying opns between meas.	Average potential difference, (volt)	Ranges of difference 0.000000 to −volt	Average deviation, millivolt	Results discarded in average
Small wires							
Shorted 0, 1–6	6	54	4	0.000002	0.000008 (.000023)	0.002	1
Shorted Au, 7–12	6	16	2	.000068	.000200	.070	0
Large wires							
Shorted A, 1–6	6	63	5	.000001	.000006 (.000007)	.001	1
Unshorted A, 1-6	6	34	2	.000001	.000005 (.000008)	.001	1
Shorted B, 1–6	6	61	5	.000001	.000004	.001	0
Unshorted B, 1–6	6	33	2	.000003	.000008 (.000039)	.002	2
Large wires							
Shorted Pt, 1–6	6	116	12	.000001	.000007	.001	0
Unshorted Pt, 1–6	6	35	2	.000002	.000008 (.000031)	.001	4
Shorted Au, 1–6	6	63	7	.000003	.000012 (.000021)	.003	2
Unshorted Au, 1–6	6	35	2	.000003	.000013	.002	0
Shorted Ir, 1–6	6	51	5	.000006	.000025	.006	0
Unshorted Ir, 1–6	6	32	2	.000007	.000033	.005	0
Shorted Rh, 1–6	6	52	5	.000002	.000011 (.000053)	.002	2
Unshorted Rh, 1–6	6	34	2	.000002	.000005 (.000012)	.001	1
Shorted St, 1–6	6	60	5	.000006	.000028 (.000034)	.006	1
Unshorted St, 1-6	6	40	2	.000006	.000014 (.000053)	.002	1
Special wires							
Shorted Am. Pt, 1–6	6	27	2	.000002	.000010	.002	0
Unshorted Am. Pt, 1–6	6	35	2	.000001	.000005	.001	0
Shorted L. & N., 1-4	4	22	2	.000000	.000001	.000	0
Foils							
Shorted P_{11-1}-P_{11-4}	4	20	2	.000001	.000005	.001	0
Unshorted P_{11-1}-P_{11-4}	4	20	2	.000001	.000006	.001	0
Shorted G_{11-1}-G_{11-4}	4	22	2	.000004	.000012	.003	0
Unshorted G_{11-1}-G_{11-4}	4	18	2	.000001	.000002	.001	0

TABLE I (Concluded)

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying opns between meas.	Average potential difference, (volt)	Ranges of difference 0.000000 to —volt	Average deviation, millivolt	Results discarded in average
Shorted P_{12-1} P_{12-4}	4	31	4	0.000002	0.000006	0.002	0
Unshorted P_{12-1}-P_{12-4}	4	20	2	.000001	.000007	.001	0
Shorted D-F	6	49	4	.000002	.000005	.002	0
Shorted G_{12-1}-G_{12-4}	4	42	6	.000001	.000006	.001	0
Unshorted G_{12-1} G_{12-4}	4	21	2	.000001	.000005 (.000012)	.001	1
Shorted P_{13-1}-P_{13-4}	4	46	4	.000002	.000008	.002	0
Unshorted P_{13-1}-P_{13-4}	4	20	2	.000001	.000003	001	0
Shorted G_{13-1}-G_{13-4}	4	35	4	.000002	.000008	,002	0
Unshorted G_{13-1}-G_{13-4}	4	20	2	.000001	,000002	001	0
Shorted P_{22-1}-P_{22-4}	4	34	4	.000001	.000004	001	0
Shorted I-N	6	44	4	.000002	.000009	.002	0
Shorted G_{22-1}-G_{22-4}	4	33	4	.000003	.000009	.002	0
Shorted P_{23-1}-P_{23-4}	4	30	4	.000001	000005	.001	0
Shorted G_{23-1}-G_{23-2}	2	5	2	.000000	.000001	.000	0

[a] Compare with Table I, Morgan, Lammert and Campbell, THIS JOURNAL, **53**, 454 (1931).

TABLE II

SUMMARY OF RESULTS SHOWING THE PERCENTAGE VARIATION IN POTENTIAL DIFFERENCES OBTAINED WHEN METALS OF DIFFERENT COMPOSITIONS AND DIMENSIONS ARE USED IN THE PREPARATION OF THE QUINHYDRONE ELECTRODE. NITROGEN USED FOR DRYING AND STIRRING

Electrode series	Number measured	Percentage of total <0 000005 volt	<0.000010 volt	>0.000010 volt
Small wires				
O, 1–6	55	85	98	2
Au, 7–12	16	6	44	56
Large wires				
A, 1–6	99	95	100	0
B, 1–6	96	88	98	2
Pt, 1-6	155	86	97	3
Au, 1-6	100	69	89	11
Ir, 1–6	83	47	80	20
Rh, 1-6	89	79	94	6
St, 1–6	102	49	74	26
Special wires				
Am. Pt, 1–6	62	84	98	2
L. & N., 1–4	22	100	100	0
Foils				
P_{11-1}-P_{11-4}	40	95	100	0
G_{11-1}-G_{11-4}	40	72	95	5
P_{12-1}-P_{12-4}	61	90	100	0

TABLE II (Concluded)

Electrode series	Number measured	Percentage of total <0.000005 volt	<0.000010 volt	>0 000010 volt
D-F	49	90	100	0
G_{12-1}-G_{12-4}	64	92	98	2
P_{13-1}-P_{13-4}	66	85	100	0
G_{13-1}-G_{13-4}	55	87	100	0
P_{22-1}-P_{22-4}	34	100	100	0
I-N	44	86	100	0
G_{22-1}-G_{22-4}	33	64	100	0
P_{23-1}-P_{23-4}	30	93	100	0
G_{23-1}-G_{23-4}	5	100	100	0

potential differences, the range of differences, and the average deviations obtained in nitrogen are much lower than those obtained in air.

Second, and a conclusion of perhaps the greatest importance, the quinhydrone electrode when prepared with c. p. platinum dipping into 0.1 N hydrochloric acid solution saturated with quinhydrone and stirred with nitrogen gives a half-cell which in our experience is more easily reproduced with great precision than any of the other half-cells used for reference. Even with the very small platinum wires (O,1–6) few potential differences (Table II) occur which are greater than 0.000010 volt; the medium sized platinum wires (A, 1–6; B, 1–6; Pt, 1–6) as well as the foils give excellent results, over 85% of the total number of cells measured giving potential differences less than 0.000005 volt and over 95% (in many cases 100%) giving differences less than 0.000010 volt. The smallest gold wires **(Au,** 7–12), as in the case of the results in air, gave erratic results and large differences; the two series of larger gold wires (Au, 1–6 and St, 1–6) and the gold foils were also less satisfactory than the platinum electrodes of the same dimensions. On the other hand, the gold electrodes purchased from Leeds and Northrup (L. & N. 1–4) were by far, as in the case of air, the most satisfactory electrodes we measured. The platinum–rhodium alloy, while less satisfactory than the pure platinum, was nevertheless more satisfactory than the platinum–iridium alloy.

Further, it is to be observed (Table I) that the potential differences obtained when the electrodes are short-circuited in pairs during pre-treatment and measurement are, in general, no smaller than when the electrodes are cleaned and dried singly. Moreover, the irregularity in the potential differences of the unshorted electrodes observed in air did not appear when the electrodes were measured in nitrogen.

What is not indicated in these tables is the very important point that whereas the cells composed of air-dried electrodes and mechanically-stirred solutions sometimes take as long as sixty minutes to reach an equilibrium potential difference, and unstirred solutions even longer, cells made with nitrogen-stirred solutions take up the equilibrium value almost immediately; the initial values are almost always very nearly the final values. That this is not due to a more efficient stirring with the nitrogen is indicated by the results obtained when air or oxygen is bubbled through the solution, results which will be discussed presently.

Our next efforts were in a direction to find out whether, if the electrodes were dried in nitrogen, it was necessary to stir the solutions with nitrogen throughout the time of measurement. We found that the average potential differences, the ranges and the average deviations were not as large as they were when the electrodes were air dried as well as measured in solutions stirred in air; on the other hand, neither were they as small as when they were measured in nitrogen-stirred solutions. This is due to the fact that when the electrodes are dried with nitrogen and the solutions mechanically stirred in the presence of air, they give small initial potential differences comparable to those obtained when nitrogen is used throughout, and larger final potential differences comparable to the equilibrium potential differences obtained when the electrodes are dried with air and the solutions mechanically stirred in the presence of air. The results which we calculated are the averages of the two types of results. Apparently, then, stirring the solution with nitrogen is of importance if the better reproducibility is desired.

Our next step was to dry the electrodes with air and to stir the solution with nitrogen. The results are given in Table III.

TABLE III

SUMMARY OF RESULTS OBTAINED WHEN THE ELECTRODES WERE DRIED WITH AIR BUT MEASURED IN SOLUTIONS STIRRED WITH NITROGEN. ELECTRODES SHORT-CIRCUITED; 0.1000 *N* HYDROCHLORIC ACID SATURATED WITH QUINHYDRONE USED

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying opns. between meas.	Average equilibrium potential, volt	Ranges of difference, 0.000000 to —volt	Average deviation, millivolt
A, 1-6	6	31	2	0.000001	0.000006	0.001
B, 1-6	6	28	2	.000002	.000010	.002
Pt, 1-6	6	32	2	.000000	.000003	.000
Au, 1-6	6	31	2	.000001	.000004	.001
St, 1-6	6	32	2	.000001	.000005	.001

Quite apparently electrodes dried in air and measured in solutions stirred with nitrogen give results fully as satisfactory as those obtained when the electrodes are dried in nitrogen as well as measured in solutions stirred with nitrogen. Consequently the more elaborate technique of drying electrodes with nitrogen may be discarded.

Some measurements were made as in the case of air with electrodes which were not dried but which were rinsed in some of the 0.1 N hydrochloric acid used and then measured in solutions stirred with nitrogen.

While the results were in general very satisfactory, they were not quite as consistent as those obtained when the electrodes were dried.

Still further measurements were made when the electrodes were dried with air and the solutions stirred with compressed air and when the electrodes were dried with oxygen and the solutions stirred with oxygen.

These methods do not give the same consistently low potential differences that are observed when nitrogen is used, which fact makes it obvious that it is the inert nitrogen which is instrumental in obviating the errors present when the half-cell is prepared in air and not an improved method of stirring the solution.

In conclusion, then, it seems fairly obvious that it is highly desirable that nitrogen be passed through the solutions during the measurements to eliminate errors which seem to arise as the result of the presence of oxygen in the solution. In the case of the gold and platinum alloys the desirability is not so marked; the action of these electrodes is erratic and demands some further study. It seems probable that the differences in air are due to the oxidation of the quinone, which introduces local disturbances in the hydroquinone–quinone equilibrium, but we are not at present able to offer any theory of the part the metal of the electrode plays in this disturbance.

Up to this time the work reported has been on the reproducibility of the different metals, in the course of which work comparisons have been made between electrodes of any one series, which is to say, in most cases, comparisons between similar specimens of the same metal. While from these results we can draw conclusions as to the relative precision with which different metals and different sizes reproduce the quinhydrone half-cell when different pieces of the same sample of metal or size are used, we cannot draw any conclusions as to whether a sample of one metal will give, within the precision of its own reproducibility when another sample of the, same metal is used, the same potential as a sample of another metal; the same may be said as to the comparative potentials of electrodes of two different sizes. Work is in progress to decide this point; it involves an intercomparison between the different series of electrodes. The results of this work will be published in the next paper.

This work was made possible by a grant from the Special Research Fund of Columbia University.

Summary

An investigation has been made of the effect of nitrogen upon the reproducibility of the quinhydrone electrode in 0.1 N hydrochloric acid, from which the following conclusions may be drawn.

1. The quinhydrone half-cell, when prepared with electrodes dried in nitrogen and with solutions stirred with nitrogen, or when prepared with electrodes dried with air and with solutions stirred with nitrogen, is far

more readily reproducible than when prepared with air-dried electrodes and solutions stirred either mechanically in the presence of air or with compressed air or oxygen.

2. In the preparation of the quinhydrone half-cell it is not sufficient to dry the electrodes with nitrogen; nitrogen must be passed through the solution. If; however, nitrogen is passed through the solution the electrodes need not be dried with nitrogen.

3. The 0.1 N hydrochloric acid quinhydrone half-cell, prepared as described in this and in the first paper of this series. is the most easily and readily reproducible electrode which the authors have used.

4. Electrodes prepared with nitrogen acquire a definite equilibrium potential much more quickly than those prepared with air.

5. Short circuiting the electrodes in pairs during pre-treatment does not affect the potential differences obtained in nitrogen.

Work is in progress which involves an inter-comparison of the electrodes of different series made up of electrodes of different metals and of different sizes of the same metal.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE ATOMIC WEIGHTS OF NITROGEN AND SILVER. I. THE RATIO OF AMMONIA TO SILVER

BY GREGORY PAUL BAXTER AND CHARLES HERBERT GREENE

RECEIVED DECEMBER 18, 1930 PUBLISHED FEBRUARY 9, 1931

Because accurate, simple and direct methods are lacking, until recently the atomic weight of nitrogen has been less certainly known than most of those of elements of low atomic weight. But in view of recent gravimetric evidence, as well as gas density and mass spectrograph measurements, there now seems to be little doubt that the value of this constant is very nearly 14.008.

This paper describes an investigation of the ratio Ag: NH_3. The ratio NO_3: Ag is already known with a higher degree of precision than most gravimetric ratios.[1] By combining the two the ratio NH_3: NO3 may be obtained. This with the assumption of the atomic weights of hydrogen and oxygen makes possible the calculation of the atomic weight of nitrogen. In spite of the fact that the method of calculating the atomic weight of nitrogen is indirect, the result is not particularly sensitive to experimental error, for an uncertainty in the ratio NH_3: NO_3 affects the atomic weight of nitrogen by a proportion only 60% greater, while a given uncertainty in

[1] 0.57479, Richards and Forbes, Pub. *Car. Inst., No.* 69, 47 (1907); Honigschmid, Zintl and Thilo, *Z. anorg. allgem. Chem., 165,284 (1927)*

the atomic weight of hydrogen affects the atomic weight of nitrogen in a proportion one-third as large.

The outline of the experimental procedure was as follows. Ammonia was weighed while adsorbed on dehydrated chabazite in a closed tube. A suitable quantity of the ammonia was then caused to evaporate into dilute hydrochloric or hydrobromic acid until the acid was exactly neutralized. The halogen content of the solution was then found by nephelometric comparison with the purest silver in the usual way.

The first step in the investigation was to make certain that the end-point in the comparison of ammonia with hydrochloric and hydrobromic acids could be determined with the necessary degree of precision. We found that this could be accomplished by using either methyl red or litmus as indicator. Approximately one normal solution of ammonium chloride, which had been subjected to one, two, three and four crystallizations from conductivity water, gave the same tint with methyl red, as nearly as could be determined, provided the crystals had been centrifugally drained and thoroughly rinsed to remove the mother liquor. The mother liquor itself was always more acid owing to escape of ammonia formed by hydrolysis.

Furthermore, if the solutions of ammonium chloride were deliberately made slightly acid or basic by addition of small amounts of hydrochloric acid or ammonium hydroxide immediately before crystallization, the crystals, if thoroughly rinsed, gave solutions of the same acidity as those of salt which had been crystallized without such additions.

The color of the indicator in 100 cc. of a normal solution of the chloride was perceptibly altered by the addition of 0.1 ml. of 0.01 normal base or acid. Since this quantity of acid corresponds to only 0.001% of the salt present, it was evident that the comparison of ammonia with hydrochloric acid could be carried out with sufficient accuracy.

Although there seemed to be every reason to expect that ammonium bromide would behave in the same manner, similar experiments were made with carefully purified ammonium bromide, without disclosing any differences, except that corresponding solutions of the bromide seemed to produce a slightly pinker shade with methyl red.

Some of the later experiments were carried out with litmus instead of methyl red. In spite of the fact that the color change of the former indicator extends over a greater P_H range, the sensitiveness of the end-point was only slightly reduced.

Although the ratio of ammonia to silver found by comparing the halide solution with the silver solution is independent of the particular halogen involved, the hydrochloric and hydrobromic acids were carefully purified. Good quality hydrochloric acid was diluted with an equal volume of water, and after the addition of a small amount of potassium permanganate to liberate bromine and iodine if present, the nearly constant boiling solution was distilled through a quartz condenser. The first half of the distillate was rejected as well as a small residue in the still. The portion retained was a second time distilled in the same way. The middle portion of the distillate was preserved in a quartz flask.

Hydrogen bromide was produced by synthesis from pure hydrogen and bromine, and the solution was further purified by distillation. Bromine was freed in large part from chlorine by solution in aqueous potassium bromide, and distillation. A portion of the partially purified bromine was converted into potassium bromide by addition to a solution of recrystallized potassium oxalate and the remainder of the bromine was subjected to a second distillation from solution in this bromide. All the product was next converted to potassium bromide by reaction with three times crystallized potassium oxalate, and after evaporation of the solution the residual potassium bromide was fused in a platinum dish with the addition of small amounts of potassium permanganate to oxidize organic matter. A concentrated solution of the bromide was boiled with a small amount of permanganate and sulfuric acid to remove residual iodine, and then the solution was cooled and treated with a considerable excess of sulfuric acid which had been heated to fuming to remove volatile acids. The potassium sulfate which deposited was separated and bromine was liberated from the solution by adding about 80% of the theoretical amount of permanganate. After distillation from the solution the bromine was washed with water and once distilled.

Hydrogen bromide was prepared by saturating pure electrolytic hydrogen with bromine at 44° and passing the mixture over hot platinized asbestos. Any excess of bromine was removed by washing the gas with ferrous bromide solution and the washed gas was then absorbed in the purest water. Two distillations of the resulting solution through a quartz condenser followed, only the middle portions of the constant boiling distillate being retained. The acid was preserved in a pyrex flask, and remained colorless.

Another specimen of hydrobromic acid was prepared by distilling a solution which resulted from work on nickelous bromide carried on by Professor S. Ishimaru.[2] The bromine used in this preparation had been subjected to the same treatment as ours. The acid seemed to have a slight tendency to decompose on standing.

Pure ammonia was prepared by fractional distillation of liquid ammonia in an all-glass apparatus constructed for the purpose by Dr. E. K. Haviland in connection with another research. The original material was commercial synthetic liquid ammonia supplied in a steel cylinder. McKelvey and Taylor[3] have shown that the important impurities in such material are

[2] Baxter and Ishimaru, THIS JOURNAL, 51, 1729 (1929).

[3] McKelvey and Taylor, *Bur. Standards, Sci. Pub. 365.*

moisture and non-condensing gases. The cylinder A (Fig. 1) was connected by means of a copper tube B to the glass purifying apparatus by means of hard de Khotinsky cement. The mercury relief valve D was long enough to permit evacuation of the apparatus. After passing through the mercury bubbler E and the trap F the gas was passed over fused potassium hydroxide in the two towers C, and through the tube H filled with the dehydrated adsorbent gmelinite, both for the removal of water, and through the sintered glass dust filter H_1 The first portion of ammonia was condensed by chilling with ether–solid carbon dioxide in L. The succeeding portions of gas were caused to bubble through the liquid ammonia in L before condensation in M. The material in L was then rejected by evaporation through the safety tube I, or through the line K, into a bottle containing dilute sulfuric acid. From M a light fraction was distilled into N which had previously been evacuated, and the remainder of the ammonia in M was condensed in O after bubbling through the liquid in N. A third similar distillation from O to Q followed. A large proportion of non-condensing gaseous impurities must have been eliminated in the three distillations. The removal of the remainder was secured by the method used by McKelvey and Taylor of condensing the ammonia as a solid by chilling S with liquid air. Uncondensed gases were then removed by exhausting S. Two more similar distillations from S to U, and from U

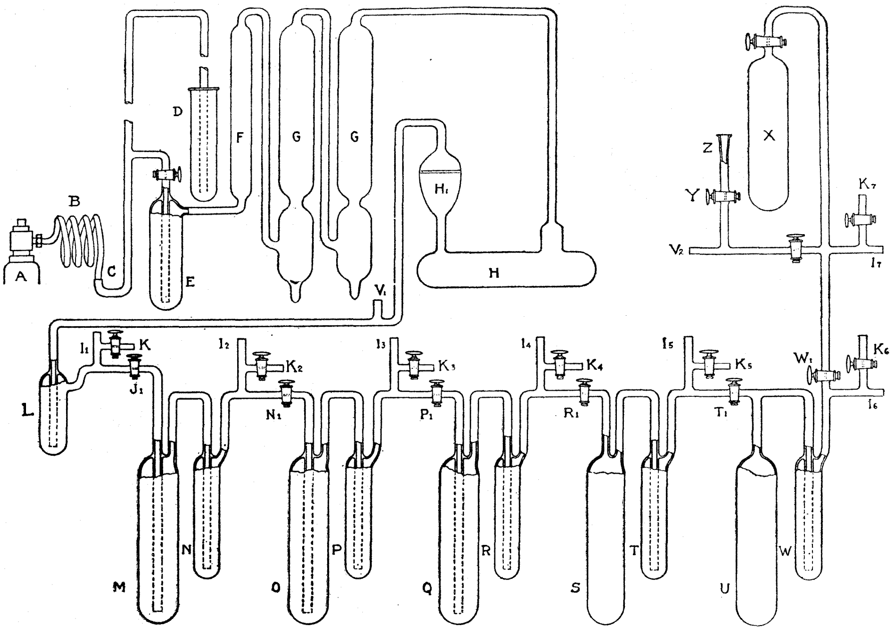

Fig. 1.—Ammonia purification train.

to X followed. In each of these distillations a light and a heavy fraction were rejected. The purified ammonia was stored in X at room temperature under pressure.

The silver used in the comparison with the ammonium halide was purified by standard methods by Dr. William *C.* Cooper for the analysis of germanium halides.[4]

The ammonia was weighed in a tube containing dehydrated chabazite (Fig. 2), provided with a well ground stopcock lubricated with rubber grease, and a sintered glass dust filter to prevent loss of chabazite powder during the expulsion of the ammonia. This chabazite had been previously employed in other experiments on adsorption. Before use in the ammonia tube it was heated to 575° in a high vacuum to eliminate so far as possible residual water and other gases to which it had previously been exposed. In the course of our experiments it was many times saturated with pure ammonia and the ammonia expelled by heating. This treatment undoubtedly removed any important amount of other gases which might not have been expelled in the initial treatment. The experiments described below to determine whether the purified ammonia still contained moisture would not have differentiated between water contained in the ammonia and that given off by the chabazite during the expulsion of the ammonia.

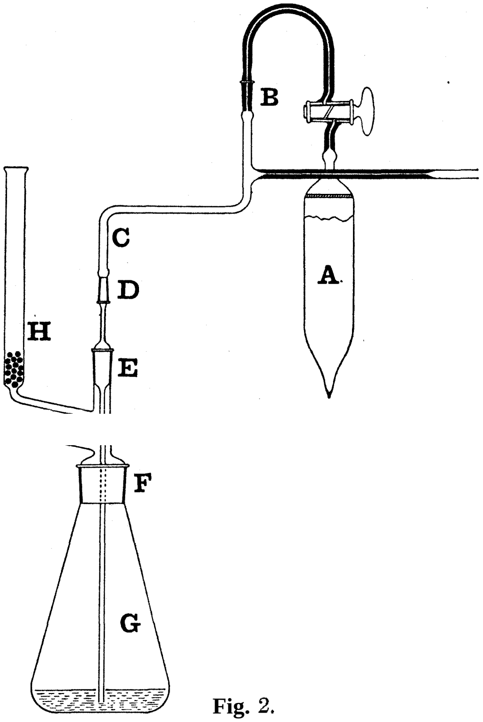

Fig. 2.

The determination of the apparently very small water content of the ammonia was a far from simple task. The method followed was to pass the ammonia expelled from the chabazite tube through a weighed tube containing freshly fused potassium hydroxide. Baxter and Starkweather[6] have found the efficiency of this substance as a drying agent to be very high, for a liter of air dried with freshly fused hydroxide even at 50° con-

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[4] Baxter and Cooper, Proc. Am. Acad., 59, 236 (1924); 60, 220 (1925); J. *Phys. Chem.*, 28, 1049 (1924); 29, 1364 (1925).

[5] Baxter and Starkweather, THIS JOURNAL, 38, 2038 (1916).

tains only 0.006 mg. of water, while at 25° the residual amount of water per liter can hardly exceed 0.002 mg. In spite of the fact that McKelvey and Taylor reject this method of determining moisture in ammonia as unreliable, we feel that it is fully as satisfactory as the one advocated by them of evolving acetylene from calcium carbide. Possibly the difficulty experienced by them with potassium hydroxide may have come from incomplete dehydration of the hydroxide at the start.

Since preliminary experiments in which rubber connections were included in the apparatus exhibited irregularities which disappeared when rubber was eliminated, the final apparatus had only sealed or ground connections. The results of the experiments in which rubber was used were not on the whole different from those with the final improved apparatus.

The procedure in the moisture determinations was as follows. A glass-stoppered U-tube containing potassium hydroxide was provided with a ground joint and a counterpoise of similar construction, volume and weight, but containing no caustic. After being wiped with first a damp and then a dry cloth, both the adsorption tube and the counterpoise were hung on a balance and left for several hours. One stopcock on each was then carefully opened and after about an hour the differences in weight were determined. The average difference between duplicate weighings was 0.014 mg. and the algebraic sum of fifteen such differences was 0.01 mg. In order to prevent diffusion of moisture into the potassium hydroxide tube while open to the air, the orifice of the outlet tube was constricted to a fine capillary. Even this did not prevent a slow but steady gain of 0.01 mg. per hour; therefore, a correction of this magnitude was applied for the period during which the tube remained open.

Both the chabazite tube containing ammonia and the absorption tube in that order were connected by greased ground joints to a line through which was flowing air which had been finally dried by means of fused potassium hydroxide.

The stopcocks of the absorption tube were then opened and ammonia was expelled from the chabazite tube through the absorption tube. Finally the chabazite tube was closed and the ammonia swept out of the absorption tube with the **air current.** Twelve similar runs in which no ammonia was involved yielded only 0.29 mg. of water in all. An average correction of −0.024 mg. was therefore applied in each experiment with ammonia. The results of the three final experiments with ammonia are given in the following table.

Wt. of NH_3	Wt. of H_2O	Wt. of H_2O corrected for blank	Per cent. of H_2O
3.14	0.00014	0.00012	0.0038
4.66	.00009	.00007	.0015
2.27	00013	.00011	.0048
Total 10.07	.00036	.00030	.0030

Another experiment with 1.42 g. of the residual liquid ammonia from a fractional distillation yielded 0.0056% of moisture.

McKelvey and Taylor[3] state that the most nearly anhydrous ammonia prepared by them contained 0.004%. At any rate it seems unlikely that any appreciable amount of water was introduced from the chabazite itself.

The quantitative comparison of ammonia with silver was conducted in the following manner. The chabazite tube charged with ammonia was carefully compared with a similar sealed counterpoise of similar exterior volume by suspending them on opposite arms of a balance in a balance room kept thermostatted within a degree or two to prevent alteration in the ratio of the lengths of balance arms. By means of the greased ground joint B (Fig. 2) the chabazite tube was connected with the tube C delivering into the Erlenmeyer flask G which contained the acid (1 normal, containing indicator) to be neutralized. Just before use this acid was further twice freshly distilled through a quartz condenser, only the middle portion being retained. The tube C delivering into the Erlenmeyer flask was connected with a supply of the purest electrolytic hydrogen. The ground joints E and F were wet with water and the guard tube H containing a few glass pearls was wet with tenth normal acid. The ground joint D was lubricated with grease.

After the apparatus had been filled with hydrogen, the chabazite tube was warmed gently with an electric oven and ammonia was allowed to flow into the hydrogen stream, except in Analysis I when the hydrogen was shut off. It was possible to determine very closely when the acid was neutralized and as soon as the end-point was nearly reached the stopcock of the chabazite tube was closed and the ammonia in the connecting tubes was swept into the flask by passing the hydrogen current for some time. The guard tube was then rinsed into the flask.

The chabazite tube was next disconnected, the ground joint cleaned with ether, and the tube again compared with the counterpoise by adding weights to the side of the balance on which the tube was hung, so that the ammonia was weighed by substitution.

To find the exact neutral point all parts of the stopper and tubes were rinsed with freshly distilled and boiled water and then the ammonium halide solution was brought to the desired shade by adding hundredth normal acid and barium hydroxide. The barium hydroxide solution had been analyzed by exactly neutralizing with hydrobromic acid and precipitating silver bromide.

In the first five experiments the standard color was produced in an acetate buffer solution which had been brought to the same shade as that given by a solution of the ammonium halide (normal). In the later experiments the standard color produced by a solution of carefully recrystallized ammonium halide was used. In Experiments 1, 2, 3, 5 and 6 methyl red dissolved in redistilled alcohol was employed, while in Experiments 10, 12, 14 and 16 a saturated aqueous solution of methyl red was substituted. For Experiments 7, 9 and 11, litmus was prepared by extracting commercial powder with hot alcohol, dissolving in water, precipitating with alcohol and dissolving in water for use. None of the indicator solutions used gave any precipitate with silver nitrate. As nearly as possible the same amount of indicator was added to the solution being titrated and to the standard color solution, and the volumes and concentrations of both were made very closely the same.

After the neutralization was complete the solution of the ammonium halide was transferred to the precipitating vessel, a 3-liter Erlenmeyer flask with a carefully ground stopper or an 8-liter bottle, and diluted. A very nearly equivalent amount of the purest silver was carefully weighed by substitution and dissolved in chlorine-free nitric acid, with especial precautions to avoid loss of spray. This solution of silver was diluted to approximately the same volume as the halide solution and then added in small portions with gentle agitation to the halide solution. The exact end-point was then found with the use of a nephelometer, by testing the supernatant liquid occasionally with equivalent amounts of halide and silver, and making up a deficiency of either by means of hundredth normal halide and silver solutions. This process always was continued for a month or more in order to allow salts occluded by the silver halide to be leached out so far as possible.

The weight of silver actually equivalent to the ammonia was found by subtracting the silver equivalent of the barium hydroxide used in the neutralizing and adding the net amount of silver used in the halide–silver comparison.

The loss in weight of the ammonia tube was corrected for buoyancy of the air on the weights and the weight of silver for buoyancy of the air on both silver and weights. For this purpose the density of the weights was assumed to be 8.3 and that of silver 10.49. The density of the air was calculated from the conditions at the time of each weighing.

In the following table the weights of ammonia are corrected for moisture content by subtracting 0.003% (page 609). The ratio $NO_3:NH_3$ is calculated assuming $NO_3/Ag = 0.57479$.'

After the earlier experiments in the above table had been completed (Analyses 1 to 7), it was evident that the ratio of silver to ammonia was lower when hydrobromic acid was used for neutralization than when hydrochloric acid was used. A search for the cause of this difference revealed the fact that in the case of hydrobromic acid the more concentrated the solutions during the precipitation, the lower the ratio. Since the silver solution was poured into the bromide solution in these experiments, a possible cause of the difficulty apparently lay in occlusion of soluble bromide by the silver bromide. To test this hypothesis in the following

TABLE I
THE ATOMIC WEIGHT OF NITROGEN
Ag = 107.880 H = 1.0078

Analysis	Concn., norm.	Acid neutr.	Indicator	Corr. wt. of NH_3 in vacuum	Wt. of Ag in vacuum	Corr. for $Ba(OH)_2$	Ag added or subtr.	Corr. wt. of Ag in vacuum	Ratio $Ag:NH_3$	Ratio $NO_3:NH_3$	At. wt. of nitrogen
1	0.09	HCl	M. R.	1.43953	9.11802	0.00000	+0.00065	9.11867	6.33448	3.64100	14.0067
2	.07	HBr	M. R.	4.67035	29.58363	.00000	− .00068	29.58295	6.33420	3.64083	14.0078
3	.06	HCl	M. R.	4.11520	26.06724	.00000	+ .00020	26.06744	6.33443	3.64097	14.0069
4	.08	HBr	M. R.	1.62620	10.30093	.00000	− .00079	10.30014	6.33387	3.64065	14.0090
5	.15	HBr	M. R.	1.85833	11.77136	.00000	− .00132	11.77004	6.33367	3.64053	14.0098
6	.09	HBr	L	1.81372	11.48867	− .00025	− .00038	11.48804	6.33397	3.64070	14.0087
7	.08	HCl	L	1.61251	10.21437	.00000	− .00040	10.21397	6.33421	3.64084	14.0078
8	.03	HBr	M. R.	1.92927	12.22401	− .00324	− .00040	12.22037	6.33419	3.64083	14.0078
9	.02	HCl	L	1.20999	7.66447	.00000	− .00021	7.66426	6.33415	3.64081	14.0080
10	.025	HBr	M. R.	1.67684	10.62236	− .00059	− .00019	10.62158	6.33428	3.64088	14.0075
11	.03	HBr	M. R.	1.89941	12.02690	− .00162	+ .00564	12.03092	6.33403	3.64074	14.0084
12	.03	HBr	M. R.	1.98867	12.59673	.00000	− .00080	12.59593	6.33385	3.64063	14.0091
Average of chlorides (1, 3, 7, 9)									6.33432	3.64090	14.0074
Average of concentrated bromides (2, 4, 5, 6)									6.33393	3.64068	14.0088
Average of dilute bromides (8, 10, 11, 12)									6.33409	3.64077	14.0082
Average of analyses 1, 3, 7, 8, 9, 10, 11, 12									6.33420	3.64083	14.0078

experiments with hydrobromic acid (Analyses 8, 10, 11, 12) the concentration of the solutions during precipitation was made from one-half to one-third that previously used. These experiments yielded results concordant with those of the earlier chlorides as well as with Experiment 9 in which the chloride solution also was made more dilute before precipitation. In Analyses 10 and 12 the bromide solution was added to the silver solution.

If the correction for water in the ammonia is omitted the ratios $Ag:NH_3$ and $NO_3:NH_3$ become 6.33401 and 3.64073, respectively, and the atomic weight of nitrogen 14.0085.

This investigation was interrupted before it was completed. It is unfortunate that a larger number of experiments could not have been carried out. The purity of the ammonia needs further investigation, especially as regards water, although the synthetic material which we used as the starting point is unlikely to be seriously contaminated with any impurities except permanent gases and moisture. On the whole the final outcome may be looked upon as valuable corroborative evidence that the atomic weight of nitrogen is very close to 14.008. The uncertainty of the method is apparently less than 0.001 unit, which compares very favorably with that of all other methods at present available for the purpose.

If nitrogen is taken as 14.0078, the atomic weight of silver may be calculated to be 107.879, while the value for nitrogen of 14.008 gives 107.880 from the $Ag:NH_3$ ratio and 107.879 from the $Ag:NO_3$ ratio.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

KINETICS OF THE POLYMERIZATION OF ETHYLENE AT PRESSURES ABOVE ONE ATMOSPHERE[1]

BY ROBERT N. PEASE[2]

RECEIVED DECEMBER 22, 1930 PUBLISHED FEBRUARY 9, 1931

Previous work[3] has indicated that the only important primary reaction of ethylene when heated in glass to 400–600° at 1 atmosphere initial pressure is one of polymerization to higher mono-olefins (C_nH_{2n}). The point has not been conclusively demonstrated, however, as would be done if a considerable portion of the ethylene could be caused to polymerize without

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[1] This paper contains results of an investigation carried out as a part of Project No. 7 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 American Petroleum Institute with the cooperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor of Princeton University is Director of Project No. 7.

[2] Research Associate, American Petroleum Institute.

[3] Day, *Am. Chem. J.*, **8,** 153 (1886); Bone and Coward, *J. Chem. Soc.*, **93,** 1197 (1908); Hague and Wheeler, *ibid.*, 390–391 (1929); Pease, THIS JOURNAL, 52, 1158 (1930); Wheeler and Wood, *J. Chem. Soc.*, 1823 (1930).

the formation of appreciable quantities of by-products such as hydrogen, methane, ethane and carbon. Examination of the experimental data reveals that the polymerization reaction at 1 atmosphere is excessively slow and apparently limited, and that it is accompanied by decomposition of the product, and probably also of ethylene itself. The indications are that the polymerization reaction is fundamentally second order, whereas the decompositions are presumably first order. The former should be favored if the initial pressure is increased. It was proposed, therefore, to study the reaction at pressures somewhat higher than 1 atmosphere. A series of experiments was carried out in which ethylene was heated in a copper bomb ta 350–500° at initial pressures of 2.5, 5 and 10 atmospheres. These experiments, the results of which are here reported, demonstrate that as much as 50% of the ethylene can be polymerized without the formation of more than 1 or 2% of hydrogen and methane. The importance of the polymerization reaction is, therefore, confirmed.

The apparatus consisted of a cylindrical copper bomb to which was connected (by means of copper tubing and suitable valves) a pressure gage, a tank of compressed ethylene and a mercury gasometer. The bomb was *20* cm. long with an outside diameter of *5* cm. Its walls were 5 mm. thick. Its volume was *250* cc. The copper tubing was **3.2** mm. internal diameter. The bomb was heated in an electric tube-heater. Temperature was measured with a double-junction chromel–alumel thermocouple, and was controlled by hand regulation of the heating current.

The bomb was flushed out five times with ethylene before and after each run. In starting a run, ethylene was allowed to flow through the bomb. The outlet was closed, and the pressure was allowed to rise to the value desired, the starting time being taken at the mid-point of filling. After some definite time interval was completed, the gases were released into the mercury gasometer. The gas was then passed through a trap at 0° to condense liquid products. A sample was analyzed for higher olefins by absorption in ordinary concentrated sulfuric acid; for ethylene by absorption in dilute bromine water; and for hydrogen plus saturated gaseous hydrocarbons by difference. The total volume of off-gas was then measured. The percentage of ethylene reacting was calculated from the volume in the off-gas, and the volume required to fill the bomb. This was compared with the amounts of higher olefin, and of hydrogen plus hydrocarbons formed.

The reaction is believed to be homogeneous as carried out, although no direct tests of the effect of increased copper surface were made. The conclusion is based on the fact that the rates are comparable with those obtained in empty pyrex glass reaction vessels, the surface of which has been shown to have a small though definite repressive action. Thus, at 500° and 1 atmosphere in glass, it was found that 14% of the ethylene reacted in twelve minutes and 19% reacted in tweoty-four minutes. In the copper bomb. at 500° and 2.56 atm. pressure, 41% reacted in fifteen minutes. This is about the expected relation if the reaction is second order (as it appears to be). Further, there was no evidence of a "drift" in the results such as might have occurred if a gradual change in the surface of the bomb due to carbonization were affecting the reaction rate.

Results

Results of the experiments appear in Table I. For each experiment there are given the temperature, the initial **pressure** of ethylene in atmospheres

Table I

Ethylene under Pressure at 350–500°

Expt	Temp., °C.	Init. press. C_2H_4, atm.	Time, hours	For 100 cc. (S. T. P.) C_2H_4 in C_2H_4 reacted, cc	Formed, cc. Gaseous C_nH_{2n}	H_2 + H. C	k_2, fraction per hour at 1 atm.
13	350	9.85	8	30.7	4.5	0	0.0056
14	375	4.83	4	23.7	7.0	0	.0161
1		9.72	1	13.8	2.9	0	.0165
12		9.80	4	37.0	8.4	0.1	.0150
15	400	4.94	2	31.7	10.5	0.3	.0470
10		9.85	1	26.9	4.0	1.6	.0374
11		9.85	2	47.9	11.6	1.0	.0467
17	425	4.90	0.5	20.3	10.8	0	.104
5		4.95	1	33.4	11.4	0.7	.101
16		4.97	2	61.5	17.3	3.0	.161
4		10.03	0.25	17.8	4.4	0.2	.086
3		9.70	0.5	34.3	6.3	0.7	.108
2		9.54	1	57.9	10.7	2.7	.144
18	450	2.52	0.5	27.0	11.3	0.3	.294
6		2.56	1	46.1	15.7	3.7	.334
8		4.95	0.25	23.1	6.1	1.5	.243
7		4.97	0.5	39.8	10.5	1.1	.266
9		9.73	0.25	42.3	11.8	1.0	.301
21	475	2.54	0.25	26.3	12.6	0.3	.457
20		2.50	0.5	48.1	16.9	2.1	.741
19		4.96	0.25	45.8	17.9	1.9	.682
22	500	2.56	0.25	41.3	15.9	3.1	1.08
23		4.87	0.25	65.1	19.8	10.9	1.53

(corrected for the nitrogen present), the time of heating in hours, and the volume in cc. (S. T. P.) of ethylene reacting, of higher gaseous olefins formed, and of hydrogen plus gaseous paraffins formed for each 100 cc. (S. T. P.) of pure ethylene introduced. The figure for ethylene is in effect the percentage of ethylene reacting. In the last column are given second order velocity constants. The numerical value of k_2 is the fraction of the ethylene which would react in one hour if the pressure of that gas were maintained constant at one atmosphere, and the reaction were actually second order. The constant is based on the following. If p is the pressure of ethylene in atmospheres and t is the time in hours

$$-\frac{dp}{dt} = k_2p^2$$

If x is fraction of ethylene converted, and p_0 is initial pressure of ethylene

$$p = p_0(1 - x)$$

Then

$$-p_0\frac{d(1 - x)}{dt} = k_2(1 - x)^2p_0^2$$

$$-\frac{d(1-x)}{(1-x)^2} = k_2p_0dt$$

$$k_2 = \frac{1}{p_0t}\cdot\frac{x}{1-x}$$

The results show clearly that it is possible to polymerize more than 50% of the ethylene to higher members of the C_nH_{2n} series without the formation of appreciable quantities of other products. The polymer is in part gaseous and in part liquid, the tendency being to form a greater proportion of the latter as reaction proceeds. In one or two favorable cases the yield of gaseous C_nH_{2n} was that to be expected from the reaction

$$2C_2H_4 \longrightarrow C_4H_8$$

It is reasonable to conclude from this fact that butylene is the primary product of the reaction.[4]

This conclusion is strengthened by an analysis of the kinetics of the reaction. If the primary reaction is that shown above, and occurs as a result of a collision in the gas phase, one would expect it to be kinetically of second order. Actually it is found that the second order constant holds reasonably well when comparisons are made between corresponding conversions at different initial pressures. Nevertheless, the constants for the most part increase as the total conversion increases. This can be qualitatively accounted for by a secondary reaction between ethylene and the butylene first formed

$$C_2H_4 + C_4H_8 \longrightarrow C_6H_{12}$$

The primary product offers an outlet for the reaction of an additional quantity of ethylene. This reaction, and the reaction

$$2C_4H_8 \longrightarrow C_8H_{16}$$

would account for the formation of the liquid products.

Bimolecular gas reactions are of special theoretical interest because it has, in general, been possible to show that the heat of activation as calculated from the temperature coefficient of the rate

$$\frac{d\ln k}{dT} = \frac{E}{RT^2}$$

can be simply interpreted as the excess of energy which two colliding molecules must possess before reaction is possible. The rate of reaction is given by the rate of collision between molecules possessing the requisite excess energy.

The case of ethylene polymerization is an exception to the rule. From the temperature coefficient of k_2, the energy of activation is calculated to be 35,000 cal.

If $Z_{\text{eff.}}$ = number of collisions per cc. per sec. between molecules possessing 35,000 cal. over the average
n = number of molecules per cc.

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[4] *See* Wheeler and Wood, *J. Chem. Soc.*, 1823 (1930), for confirmation.

σ = molecular diameter in cm.

$\bar{c}$ = root mean square velocity in cm. per sec.

then $Z_{\text{eff.}} = \sqrt{\frac{2}{2}}\, n^2 \pi \sigma^2 \bar{c}\, e^{-35,000/RT}$

k_2 = fraction of molecules reacting per hour when the pressure is maintained at 1 atm.

$k_2 = 2.3600 \cdot Z_{\text{eff.}}/n$

n = number of molecules per cc. at 1 atm. press.

$k_2 = 3600 \sqrt{2}\; n\; \pi \sigma^2 \bar{c}\, e^{-35,000/RT}$

The observed value of k_2 at 425° is 0.1. The calculated value is

$$k_2 = 3600 \cdot \sqrt{2} \cdot 1.058 \times 10^{19} \pi\, (3.78 \times 10^{-8})^2\, 78810\, e^{-35,000/4.58 \cdot 698} = 215.$$

The observed value is thus only $^1/_{2000}$ of that calculated. If, instead of calculating k_2 at 425°, we use the observed value of k_2 at 425° to calculate the heat of activation, the latter comes out to be 45,650 cal. This corresponds to a temperature coefficient of 3.1 per 25°, whereas the observed value is *2.3* per 25°.

There is no question as to the existence of a wide discrepancy between the observed rate and that to be expected on the basis of the collision theory. It is true that the variation in the values of k_2 at each temperature allows some latitude of choice of temperature coefficient, but even the extreme value would not be sufficiently high. The low rate of formation of product cannot be due to a reverse reaction because the discrepancy between observed and calculated rate is far too large. The reverse action would have to be more than 1000 times the faster, under which conditions no reaction whatever would be observed.

The cause of the discrepancy is undoubtedly to be sought in the type of reaction under investigation. The ethylene polymerization is an association reaction taking place in the gas phase. It is not immediately obvious how such a reaction can be of second order at all. Theoretical considerations based on the older quantum mechanics rule out the possibility that a stable product molecule can be formed as the immediate result of a collision between two active reactant molecules.[5] The argument is simple. The energies of the reacting molecules and the heat of reaction must be suitably represented in the product molecule. However, the translational energy of the latter with respect to that of the reactant molecules is limited by the requirements of the law of conservation of momentum, while its rotational and vibrational energy is limited by quantum restrictions. Since the energy to be accommodated in the product molecules may have any value whatsoever, the chance that it can be exactly accommodated in any particular collision under these restrictions is negligible. Hence, reaction is highly improbable. Prior to the introduction of the quantum theory there would have been no such difficulty. Now with the development of the uncertainty principle, the above argument

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[5] See, *e. g.*, Born and Franck, *Ann.*, [4] *76, 225 (1925).*

seems to lose some of its force. If, by specifying that two molecules collide, we virtually specify their positions, then their momenta become to a degree uncertain, and as a consequence there will always exist a finite though usually small probability of accommodation and therefore of successful reaction between suitably activated molecules. The average of these probabilities over all activating collisions would be given by the ratio of the reaction rate to the rate of occurrence of such collisions. In the case of ethylene polymerization, the latter has been calculated to be about 1 to 2000.

There are three alternatives to the mechanism just presented. The difficulty as to the accommodation of the energy of reactant molecules plus the heat of reaction in the product molecule may be solved by radiation of a part of the energy, or by transfer at the reaction vessel walls, or by a suitable distribution of energy between the product molecule and a third molecule which enters into the collision. Radiation by molecules of this type has not a high degree of probability. Wall reaction seems to be ruled out by the observation that a glass packing diminishes the rate somewhat. This leaves us with the possibility of termolecular collisions. The immediate objection to this latter is that it would appear to require that the reaction be of third order rather than second. However, this may not be a disadvantage since at 1 atmosphere there is some evidence of a fall in rate more rapid than would be expected of a second order reaction. Professor H. S. Taylor has suggested a mechanism which appears capable of presenting this view of the reaction. This is given below.

Assume that a quasi-molecule, C_4H_8, is formed as a result of collision between two ethylene molecules. This complex can have only an excessively short life. It may immediately resolve itself into two ethylene molecules, or it may be decomposed by collision with an ethylene molecule, or finally it may be stabilized by a collision with an ethylene molecule. We thus have

$$2C_2H_4 \xrightarrow{k_1} C_4H_8'$$

followed by

either, $C_4H_8' \xrightarrow{k_2} 2C_2H_4$

or, $C_4H_8' + C_2H_4 \xrightarrow{k_3} 3C_2H_4$

or. $C_4H_8' + C_2H_4 \xrightarrow{k_4} C_4H_8 + C_2H_4$

For the rates of these reactions, we write

$$+\frac{d[C_4H_8']}{dt} = k_1[C_2H_4]^2$$

$$-\frac{d[C_4H_8']}{dt} = k_2[C_4H_8'] + k_3[C_4H_8'][C_2H_4] + k_4[C_4H_8'][C_2H_4]$$

If we assume that the concentration of C_4H_8' has a steady-state value, we can write

$$k_1[C_2H_4]^2 = k_2[C_4H_8'] + k_3[C_4H_8'][C_2H_4] + k_4[C_4H_8'][C_2H_4]$$

Whence

$$[C_4H_8'] = \frac{k_1[C_2H_4]^2}{k_2 + k_3[C_2H_4] + k_4[C_2H_4]}$$

Finally

$$+\frac{d[C_4H_8]}{dt} = k_3[C_2H_4][C_4H_8']$$

$$= \frac{k_1k_3[C_2H_4]^3}{k_2 + k_3[C_2H_4] + k_4[C_2H_4]}$$

When the ethylene concentration is high, this reduces to

$$+\frac{d[C_4H_8]}{dt} = \frac{k_1k_3}{k_3 + k_4}[C_2H_4]^2$$

which is the second order form. With suitable values of the temperature coefficients of the various velocity constants involved, the experimentally observed coefficient could be fitted. At very low concentrations of ethylene, the equation becomes

$$+\frac{d[C_4H_8]}{dt} = \frac{k_1k_3}{k_2}[C_2H_4]^3$$

that is, the reaction is third order.

Summary

The rate of polymerization of ethylene has been measured at 2.5, 5 and 10 atmospheres from 350 to 500°. At least 50% of the ethylene may be polymerized to gaseous and liquid mono-olefins without the formation of more than a few per cent. of hydrogen and saturated hydrocarbons.

The reaction is of second order and has an abnormally low temperature coefficient. This is discussed in the light of the fact that the reaction is of the association type.

PRINCETON, NEW JERSEY

NOTES

A Note on Diffusion in Gelatin Gels.—In a recent paper on the diffusion of non-electrolytes in gelatin gels, Friedman and Kraemer[1] have observed that the coefficient of diffusion is diminished by an increase in the concentration of the gel. A similar diminution was observed by Stiles and Adair,[2] who found that the coefficient of diffusion of sodium chloride decreased from 0.675×10^{-5} in a 4% gel to 0.483×10^{-5} in a 16% gel.

The results of Friedman and Kraemer are consistent with the formula we published, to show the relation between coefficient of diffusion and gel concentration. The formula is

$$k = a(1 - bc)$$

where k is the diffusion constant of sodium chloride in the gelatin gel, c is concentration of gelatin in percentage by weight, a is a constant = 0.74

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[1] L. Friedman and E. O. Kraemer, THIS JOURNAL, 52,1295 (1930).

[2] W. Stiles and G. S. Adair, *Biochem. J.*, 15,621 (1921).

$\times 10^{-5}$ at 0°, and 1.35 $\times 10^{-5}$ at 20°, and b is a constant, approximately 0.018.

The range of application of this formula is restricted to systems containing from 2 to 16% of gelatin. The constant b is a measure of the effect of the gelatin in arresting diffusion. In our experiments with sodium chloride the term b appeared to be practically constant. The values calculated from the data for urea, given by Friedman and Kraemer, show very considerable irregularities; one experiment gave a result for *b* which was the same as ours, but another gave a higher value, nearly 10 times as great. Their experiments with glycerol and with sucrose gave values for b of about 0.034 and 0.058, respectively. It is interesting to note that the values of b obtained with non-electrolytes are of the same order of magnitude as those obtained by us with sodium chloride.

It seems desirable to draw attention to the essential agreement of the results obtained in both investigations, because the following passage occurs in Friedman and Kraemer's paper: "A decrease in the rate of diffusion of 20% as the concentration of the gel increased from 2.5 to 5% is shown, contrary to the statement by Stiles and Adair that above 2% there is very little change." Their abbreviated quotation conveys an entirely different meaning from the actual statement of Stiles and Adair, namely, "with concentrations above 2% the curve connecting the coefficient of diffusion and concentration is approximately a straight line, the rate of decrease of the diffusion coefficient with increasing concentration of the gel being less than with concentrations less than 2%."

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RECEIVED JUNE 26, 1930
PUBLISHED FEBRUARY 9, 1931

Glass Electrode Measurements by Means of a Galvanometer with Condenser Attachment.—Due to the high resistance of glass electrodes and to a possible polarization of their membranes on the passage of a direct electrical current, e. m. f. measurements of glass electrode potentials have hitherto not been carried out with the ordinary galvanometer–potentiometer systems. Jones and Kaplan have recently invented a condenser galvanometer system which enables potential measurements on cells of high resistance to be made with a ballistic galvanometer.[1] By means of

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[1] Grinnell Jones and B. B. Kaplan, THIS JOURNAL, 50, 1853 (1928); see W. E. L. Brown, J. *Sci. Instruments*, 2, 12 (1924), for a brief mention of a similar arrangement. H. T. Beans and E. T. Oakes, THIS JOURNAL, 42, 2116 (1920), and H. T. Beans and G. H. Walden, Jr., *ibid.*, 50, 2673 (1928), have used a condenser for making potential measurements, but as their method is not a null-point method it was not used here.

this instrument it is now possible to test the applicability of galvanometers to glass electrode measurements and to test the question of membrane polarization.

Through the courtesy of Professor Jones, the same apparatus that he and Kaplan used was made available for this research; the details of operation and manipulation are fully described in their paper and need not be repeated here. Similarly, the glass electrode technique has already been given by MacInnes and Dole.[2] In Table I a typical example of a cell reading is given. There was no indication of any drift of potential due to polarization of the electrodes by the current charging the condenser.

TABLE I

MEASUREMENT OF A GLASS ELECTRODE CELL USING THE CONDENSER ATTACHMENT

Potentiometer setting. volt	Time allowed for condenser to charge, seconds	Galvanometer deflections on scale, millimeters
0.44	15	L, 10.0
.43	15	L, 2.0
.42	15	R, 3.0
,427	30	L, 1.0
.426	30	L, 0.1
.4258	60	0
.4258	120	R, 0.2
.4260	120	L, .2

Accepted potential 0.4259 L = left. R = right

In Table II are given the asymmetric potentials and resistances of the glass electrodes used in the final measurements. One electrode was prepared from glass furnished by the Corning Glass Company (their 0.012 glass) and the other from glass made in the manner described by MacInnes and Dole.

TABLE II

ASYMMETRIC POTENTIALS AND RESISTANCES OF GLASS ELECTRODES USED

	Asymmetric potentials, volt	Resistances, megohms
Corning glass	−0.0010	51.5
MacI.–D. glass	− .0020	21.1

The hydrogen half-cell and the glass electrode half-cell were measured in two solutions of different PH against a saturated calomel reference electrode at 27.3°. The solutions were made up only approximately.

The final measurements are given in Table III. The hydrogen–calomel cell was measured without using the condenser. From the last column of Table III it is evident that both Corning glass electrodes and MacInnes and Dole glass electrodes give the correct hydrogen electrode potential changes as measured with the ballistic galvanometer–condenser system.

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[2] D. A. MacInnes and Malcolm Dole, *Ind. Eng. Chem. (Anal. Ed.)*, 1, 57 (1929); THIS JOURNAL, 52, 29 (1930).

TABLE III

COMPARISON OF HYDROGEN AND GLASS ELECTRODE POTENTIALS USING THE GALVANOMETER WITH CONDENSER ATTACHMENT

Electrode (against calomel)	Potentials in volts Solution 0.1 *N* HCl	0.1 N Na_2HPO_4	*AE*
Hydrogen (1)	0.3084	0.7780	0.4696
Hydrogen (2)	.3084	.7778	.4694
Corning glass	– .0433	.4261	.4694
MacI.-D. glass	– .0425	.4268	.4693

There is again no evidence of polarization and the results are as accurate as can be obtained with other methods of glass electrode measurements.

CONTRIBUTION FROM THE
CHEMICAL LABORATORIES OF
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RECEIVED SEPTEMBER 30, 1930
PUBLISHED FEBRUARY 9, 1931

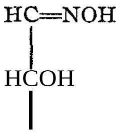
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE REACTIVE FORM OF GLUCOSE OXIME[1]

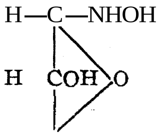
BY M. L. WOLFROM AND ALVA THOMPSON

RECEIVED JUNE 23, 1930 PUBLISHED FEBRUARY 9, 1931

The fact that glucose reacts with hydroxylamine to form an oxime has been used as proof for the presence of an aldehyde group in the molecule of this sugar. Glucose oxime was first prepared in crystalline form by Jacobi[2] and its structure was tacitly assumed to be of the true oxime type, R—CH=NOH. The establishment of the ring or cyclic hemiacetal structure for the crystalline forms of glucose raised the question whether this ring opened or remained intact in the nitrogen condensation products of the sugar. In the case of the oxime, these two possibilities are illustrated as follows



True oxime



Ring type oxime

Each of the above types could exist in two isomeric forms, *syn* and *anti* in the true oxime structure and alpha and beta in the other. In the latter case, the formation of more than one ring would indeed give rise to further isomers, but this possibility is not pertinent to the following discussion

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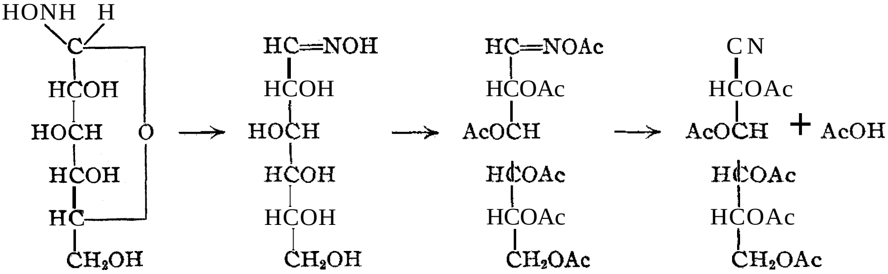
[1] (a) Constructed from a thesis presented by Alva Thompson in candidacy for the degree of Doctor of Philosophy in Chemistry at The Ohio State University. (b) Presented before the Division of Organic Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Georgia, April 7 to 11, 1930.

[2] H. Jacobi, *Ber.*, 24, 697 (1891).

and may be disregarded. Furthermore, the exact location of the lower end of any oxygen bridge present need not concern us.

Evidence as to the type of structure of the one known crystalline form of glucose oxime was produced by Miller and Plöchl,[3] who found that glucose oxime did not add hydrogen cyanide, as is characteristic of a true oxime. The objection may be raised that this result is based upon negative experimental data, but positive evidence pointing to the same conclusion was obtained by Irvine and Gilmour.[4] These workers found that on methylation and hydrolysis of this compound, crystalline tetramethylglucose of the lactal or ring structure was obtained instead of the open-chain pentamethylglucose,[5] as would be the case if the substance were a true oxime.

Although the lactal structure for glucose and its derivatives explains many of the reactions of this important compound, it has been postulated by one of us[6] and by others that in many reactions, and especially in those of a deep-seated nature, the glucose molecule reacts in the open-chain form. The lactal structure may then be considered as a resting or passive phase in these reactions, the ring opening to produce the highly reactive open-chain form as needed. The importance of this molecular behavior in biological reactivity is obvious. In the work herein reported we have verified this assumption by working with a nitrogen derivative, the oxime. The deep-seated reaction we have chosen to study is the formation of the acetylated nitrile from the oxime. This is the first step in the well-known Wohl sugar degradation. The agents used for this change are sodium acetate and acetic anhydride at relatively high temperatures. The end result of this reaction is, of course, an open-chain compound, but the point in question is whether the lactal structure opens to form the straight chain or true oxime as an intermediate, as follows



It is to be noted that the first reaction above is in the nature of a hydrogen shift and would probably be a prototropic change. Whether this is

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[3] W. v. Miller and J. Plöchl, *Ber.*, **27**, 1281 (1894)

[4] J. C. Irvine and R. Gilmour, J. *Chem. Soc.*, 93, 1429 (1908); *cf.* J. C. Irvine and Agnes Moodie, *ibid.*, **93**, 95 (1908).

[5] P. A. Levene and G. M. Meyer, J. *Biol. Chem.*, 69,175 (1926).

[6] *M.* L. Wolfrom, THIS JOURNAL, **51**,2188 (1929).

a true tautomeric phenomenon or whether it is a definite change is still open to question.

The isolation of the open-chain or aldehydo form of glucose penta-acetate[6] has made possible the synthesis of the third compound represented above, as a reference substance for the study of this reaction.[7] Aldehydo-glucose penta-acetate[8] gave a crystalline oxime penta-acetate on reaction with hydroxylamine. Further acetylation yielded the crystalline hexa-acetate, which was isolated in two forms with melting points of 79 and 119.5°, respectively. The lower-melting compound was the form obtained first. This was very unstable and changed spontaneously into the other, after which all attempts to gain the 79° isomer failed. This latter substance showed a characteristic behavior on melting, first fusing at 79°, then, on continued heating, re-solidifying and again melting at about 119°. We believe that these isomers are probably syn and anti forms, although the possibility of an unstable pseudomorph has not been excluded, due to the fact that we failed to obtain the optical rotation of the 79° form.

In his classical work on the degradation of glucose, Wohl[9] isolated an oxime hexa-acetate in the mother liquor from the crystallization of the acetylated gluconic acid nitrile. He gave the melting point of 109–110° for this compound and stated that it did not undergo nitrile formation. He considered this to be the anti form of the acetylated oxime and happily attributed the rather low yield of acetylated nitrile to the fact that half of the oxime was in this form which did not give the nitrile. Behrend[10] obtained this same hexa-acetate by low temperature acetylation of glucose oxime with acetic anhydride and pyridine. He gave the melting point of 110–111° for this compound and showed that it possessed a normal molecular weight. We have repeated and confirmed the work of these two investigators. On rigorous purification of this compound we have obtained for this substance the melting point of 113–115° and the specific rotation of +7° in U. S. P. chloroform solution. The rotation of this substance has not been previously recorded. Behrend and Roth[11] had used this method of mild acetylation to correlate the two lactal penta-acetates of glucose with the two alpha and beta forms of the free sugar, which indicates that this treatment did not alter the lactal nature of the compound. Since Irvine and Gilmour[4] have later shown that glucose oxime has a ring

[7] Recently P. Brigl and H. Muehlschlegel, ***Ber.***, 63, 1551 (1930), have prepared aldehydo-d-glucose pentabenzoate mono-ethyl alcoholate from glucose mercaptal pentabenzoate by hydrolysis with formic acid. These authors use the prefix *al-* to denote the aldehydo form.

[8] M. L. Wolfrom, THIS JOURNAL, 52, 2464 (1930).

[9] A. Wohl, Ber., 26, 730 (1893).

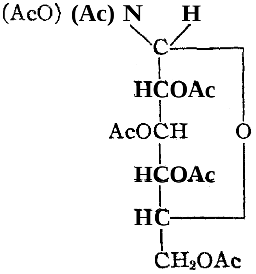
[10] R. Behrend, ***Ann.***, 353, 106 (1907).

[11] R. Behrend and P. Roth, ibid., 331, 359 (1904).

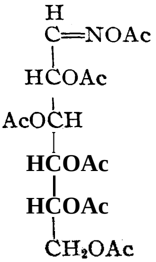
structure, then it follows that this hexa-acetate also is the ring form. From their low rotations, these substances are very probably the beta isomers, according to the general classification of Hudson.[12] The constants of glucose oxime are given by Irvine and Gilmour[4] as follows: m. p., 138°; specific rotation in aqueous solution, −7.8°, changing to the final value of —0.8'. By rigorous purification we have found the melting point of 142–143° and the specific rotation in 4% aqueous solution of −8.9°, changing to the final value of −2°.

The second oxime hexa-acetate of glucose which we have now obtained has widely differing constants from the one previously known. The melting point is 119.5° and the specific rotation in U. S. P. chloroform solution is +46°. From its method of synthesis it possesses the true oxime structure. On heating with acetic anhydride and sodium acetate it readily yielded the acetylated nitrile. On heating this hexa-acetate in the solid form to 135–140°, it began to decompose into acetic acid and acetylated nitrile. The sirup so obtained was colorless and gave a good yield of pure gluconic acid nitrile penta-acetate. These experiments show that this form of acetylated glucose oxime can lose acetic acid to form the acetylated nitrile, whereas the acetylated ring form of the oxime does not possess this property. It is of interest to note here that the penta-acetate of aldehydo-glucose oxime does not form the acetylated nitrile on heating. This indicates that acetic acid and not water is split out in the reaction.

To distinguish the ring form of the acetylated oxime from the open-chain form, the name 0-glucose oxime hexa-acetate is suggested for the former, the prefix denoting the beta ring structure. In a parallel way, the prefix aldehydo is suggested for the other isomer, this prefix denoting the open-chain form. The differing structures for these two substances are illustrated by the following formulas



β-Glucose oxime
hexa-acetate



Aldehydo-glucose
oxime hexa-acetate

On repeating Wohl's[9] procedure, we have confirmed his finding that at 135° or slightly above the reaction produces gluconic acid nitrile penta-acetate in about 40% yield, together with a small amount of the 0-glucose

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[12] C. S. Hudson, This Journal, 31, 66 (1909).

oxime hexa-acetate. In this latter compound it is seen that the active hydrogen atom that is attached to nitrogen and is concerned in the shift to the aldehydo structure is here replaced by an acetyl group, which in this case blocks any change to the open-chain form. This compound is thus produced by direct acetylation of the ring form of glucose oxime before the ring has opened.

Gluconic acid nitrile penta-acetate has been rigorously purified and we have found the melting point of 83–84' and the specific rotation in U. S. P. chloroform solution of +48°. This optical rotation has been recorded for the first time.

By using Wohl's procedure, but keeping the reaction temperature below 90°, aldehydo-glucose oxime hexa-acetate, melting point 119.5°, was formed from *β*-glucose oxime and was isolated along with a low yield of acetylated nitrile. This would seem to be definite proof that this open-chain acetate is an intermediate in the reaction. The ring form of glucose oxime then opens and undergoes acetylation, followed by the loss of acetic acid from the acetylated open-chain or true oxime form.. We believe the experimental data reported confirm this statement. The reaction as a whole is a complicated one, as is indicated by the low yield, 40%, of acetylated nitrile formed under the best conditions known. The above mechanism may not account for the entire reaction, but it would certainly appear that it accounts for some of this yield of acetylated nitrile and perhaps for the major part of it. We are not interested in explaining the exact mechanism of this reaction, but only in proving that a shift from a lactal structure to the aldehydo or open-chain form does take place.

The question of the stability of the non-acetylated aldehydo-glucose oxime is of interest. Aldehydo-glucose oxime penta-acetate underwent hydrolysis on acid de-acetylation. A basic de-acetylation using methyl alcohol and ammonia produced only the previously known @-glucose oxime, thus showing that when the hydrogen atom concerned in the change between the two forms is not blocked, the solid phase separating from the solution is the ring form. In this connection it is to be noted that *β*-glucose oxime undergoes mutarotation, whereas none of the oxime acetates we have studied mutarotate, even in the presence of dry hydrogen chloride. In the case of these acetates the mobile hydrogen atoms are replaced by acetyl groups.

Recently, Busch and Kämmerer[13] have isolated the crystalline pseudo oxime form of phenacyl-p-toluidine oxime, $C_6H_5C(NHOH)=CHNH-C_6H_4CH_3$. This is analogous to an enolic form. The possibility of such a pseudo oxime being a factor in the work herein reported is easily eliminated with sugar derivatives. Such a substance should produce both gluconic and mannonic acid nitrile penta-acetates, as it is known that the shift from

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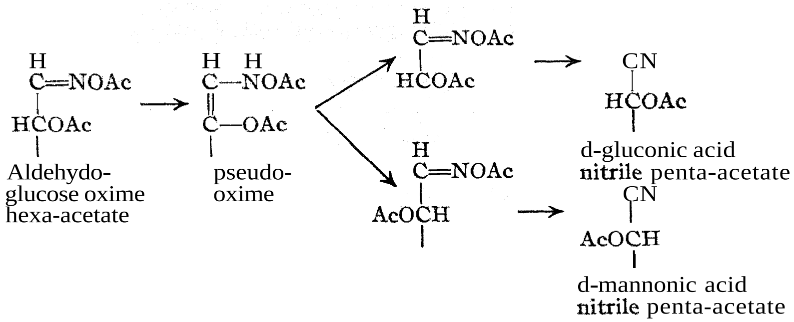
[13] M. Busch and R. Kämmerer, *Ber.*, 63, 649 (1930).

a double bond linkage to a new asymmetric carbon atom would produce both forms,[14] as is illustrated below



The acetate of mannonic nitrile was not known. It was accordingly synthesized and found to be readily distinguishable from the acetate of gluconic nitrile. It was not found in the reactions studied and it then follows that no consideration of pseudo oxime forms need be made.

Further work on the synthesis and reactivity of the open-chain forms of sugar acetates is in progress in this Laboratory.

Experimental

A.—Synthesis and Preparation of Reference Compounds

Aldehyde-glucose **Oxime** Penta-acetate.—Ten grams (1 mole) of aldehydo-glucose penta-acetate was added quickly to 100 cc. of boiling water, the solution filtered and cooled as rapidly as possible to room temperature. To this solution was added a mixture of 2.3 g. (1.3 moles) of hydroxylamine hydrochloride and 5 g. (2 moles) of potassium acetate in the dry form. In a few minutes the solution became milky and the oxime separated as an oil. The mixture was allowed to stand at room temperature and was then placed in the ice box to crystallize. The crystalline material was filtered and washed with water; yield, 7.3 *g.*; m. p. 95–97°. It was recrystallized by dissolving in the smallest possible quantity of methyl alcohol and adding water to opalescence. Crystals separated after standing overnight in the ice box. These were filtered and washed with cold water, m. p. 95–97". After another recrystallization in the same manner, the substance melted at 97–98° and gave a polarization value of $[a]^{28}_{D}$ +57.4° (0.2104 g. of subs., 10.06 cc. of U. S. P. chloroform soln., α = +1.32°, 1.1-dm. tube). After two more recrystallizations the m. p. was 99–99.5° and $[\alpha]^{24}_{D}$ +57.2° (0.2096 g. of subs., 10.06 cc. of U. S. P. chloroform soln., α = +1.31°, 1.1-dm. tube) was obtained. No rapid or appreciable mutarotation was observed in methyl alcohol solution containing 0.005% of dry hydrogen chloride. Under these conditions the anilides of tetramethylglucose and tetramethylmannose will mutarotate to a constant value.[14] The polarization value of the substance in pure methyl alcohol was $[\alpha]^{24}_{D}$ +49.9° (0.3487 g. of subs., 10.02 cc. of methyl alcohol soln., α = +1.91°, 1.1-dm. tube). A second value was $[\alpha]^{24}_{D}$ +49.7° (0.3456 g. of subs., 10.06 cc. of methyl alcohol soln., **a** = +1.71°, 1.0-dm. tube).

The substance at room temperature is soluble in ethyl alcohol, very soluble in methyl alcohol, acetone and chloroform, but is practically insoluble in water and petro-

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[14] M. L. Wolfrom and W. Lee Lewis, THIS JOURNAL, 50, 837 (1928).

leum ether. It is soluble in hot water but is practically insoluble in hot petroleum ether. It crystallizes in massive six-sided plates.

Anal. Subs., 0.2635: N_2, 9.03 cc. (749.5 mm., 23"). Calcd. for $C_6H_8O_5N(CH_3CO)_5$: N, 3.45. Found: N, 3.76. Calcd. for acetyl, 0.2000: 24.7 cc. 0.1 *N* NaOH. Found: 24.7 cc.

Aldehyde-glucose Oxime Hexa-acetate.—Thirty cubic centimeters of acetic anhydride was added to a solution of 10 g. of aldehydo-glucose oxime penta-acetate in 60 cc. of dry pyridine at 0°, and allowed to stand in an ice-bath for one hour. It was then poured into five times its mass of ice and water and stirred until all the acetic anhydride had been hydrolyzed. The mixture was then extracted with 50 cc. of chloroform. The chloroform solution was washed successively with a 3% sulfuric acid solution, saturated sodium bicarbonate solution and water, all solutions being kept near ice temperature. The chloroform solution when evaporated left a thick sirup which was crystallized by dissolving in the smallest possible volume of 95% ethyl alcohol and adding water to opalescence. The crude yield was 8.9 g. After one recrystallization the substance melted sharply at 79°; as the bath was heated, it solidified and melted again at 119°. After two recrystallizations, it melted at 119.5°. After four recrystallizations it melted at 119.5" and gave a polarization value of $[\alpha]_D^{28}$ +46.3° (0.4043 g. of subs., 10.06 cc. of U. S. P. chloroform soln., a = +2.05°, 1.1-dm. tube). After five recrystallizations the m. p. was 119.5° and the polarization value $[\alpha]_D^{25}$ +45.9° (0.4022 g. of subs., 10.06 cc of U. S. P. chloroform soln., a = +2.02°, 1.1-dm. tube) was obtained. The polarization value of the pure substance in methyl alcohol was $[\alpha]_D^{26}$ +40.9° (0.2010 g. of subs., 10.06 cc. of methyl alcohol soln., α = +0.90°, 1.1-dm. tube). A second value was $[\alpha]_D^{24}$ +41.0° (0.2029 g. of subs., 10.06 cc. of methyl alcohol soln., a = +0.91°, 1.1-dm. tube). No rapid or appreciable mutarotation was observed in methyl alcohol solution containing 0.005% of dry hydrogen chloride.

The substance is soluble in hot ethyl alcohol and hot water. It is practically insoluble in cold alcohol, water, petroleum ether and ether but is soluble in cold acetone.

Anal. Subs, 0.3030: N_2, 9.4 cc. (760 mm., 26°). Calcd. for $C_6H_7O_6N(CH_3CO)_6$: N, 3.14. Found: 3.42. Calcd. for acetyl, 0.1000: 13.4 cc. 0.1 *N* NaOH. Found: 13.6 cc.

The acetyl value was determined by distilling 0.5 g. of the substance with 50 cc. of 20% sulfuric acid, water being added to replace that lost by distillation. The acetic acid was then determined in the distillate by titration.

For purposes of identification, a crystallographic description of this compound was made by Doctor V. H. Morris of the Ohio Agricultural Experiment Station.

Crystallographic Description of **Aldehydo-d-glucose-oxime** Hexa-acetate (119.5° Form).—The crystal is observed as colorless elongated prisms belonging to the orthorhombic system. The elongation is in the direction which is taken as crystallographic *c*. The crystal is characterized by the common occurrence of pyramid faces on one or both ends. The optical sign of the crystal is negative; the indices of refraction are a = 1.460, β = 1.497 and γ = 1.504. Interference colors vary from first order gray when the acute bisectrix emerges, to third and fourth order colors when the optic normal emerges. The crystal shows parallel extinction in all positions. Since the vibration direction of (γ) is parallel to the direction of elongation, the sign of elongation is positive. The optic plane is parallel to the direction of crystallographic *c* and normal to one of the edges between two prism faces. When the crystal is observed lying on one of the edges between two of the prism faces, the acute bisectrix emerges; in this position beta (β) can be measured across the crystal and gamma (γ) along the elongation. When the crystal is observed lying on the edge between the other two prism faces, the optic normal emerges; in this position alpha (a) can be measured across the crystal and gamma (γ) along the elongation. The optic angle is small. The vibration direction of the obtuse bisectrix is the direction of crystallographic c, the direction of elongation.

Properties of β-Glucose Oxime Hexa-acetate.—&Glucose-oxime hexa-acetate was prepared by the method of Behrend.[10] It was crystallized by dissolving the thick sirup obtained in ethyl alcohol and adding water to opalescence. After three crystallizations the m. p. was 113–115° and the polarization value was $[\alpha]^{25}_{\mathrm{D}}$ +7.3° (0.4014 g. of subs., 10.06 cc. of U. S. P. chloroform soln., a = +0.32°, 1.1-dm. tube). After four crystallizations the m. p. was 113–115°, and the polarization value was $[\alpha]^{25}_{\mathrm{D}}$ +7.3° (0.4018 g. of subs., 10.06 cc. of U. S. P. chloroform soln., a = +0.32, after forty-eight hours, 1.1-dm. tube). In methyl alcohol the rotation of the pure substance was $[\alpha]^{24}_{\mathrm{D}}$ −1 3° (0.4026 g. of subs., 25.00 cc. of methyl alcohol soln., α = —0.04". 2-dm. tube). Another determination gave the value $[\alpha]^{27}_{\mathrm{D}}$ —1.3' (0.4042 g. of subs , 25.00 cc. of methyl alcohol soln., a = −0.04°, 2-dm. tube). From its low rotation the substance is probably the beta form. No rapid or appreciable mutarotation was observed in a methyl alcohol solution containing 0 005% of dry hydrogen chloride.

The substance is soluble in methyl alcohol, ethyl alcohol, chloroform and acetone, but is practically insoluble in ether, petroleum ether and water at room temperature. It is slightly soluble in hot water, but insoluble in hot petroleum ether. It crystallizes in fine needles. The substance was analyzed, as no analysis was found recorded in the literature.

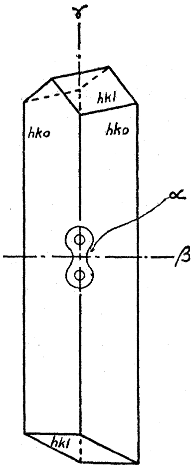

Fig. 1.—Optical orientation of aldehydo-*d*-glucose oxime hexa-acetate, 119.5" form.

Anal. Subs., 0.3045: N_2, 9.8 cc. (731.3 mm., 32°). Calcd. for $C_6H_7O_6N(CH_3CO)_6$: N, 3.14. Found: N, 3.28. Calcd. for acetyl, 0.5004: 67.0 cc. 0.1 N NaOH . Found: 67.3 cc. The acetyl value was determined as described for aldehydo-glucose oxime hexa-acetate.

Preparation of **Mannose Oxime.**—The directions of Fischer and Hirschberger[15] were slightly modified to give a more convenient method of preparation. Ten grams of mannose was dissolved in 15 cc. of water. To this solution was added a mixture of 15 g. of potassium acetate and 7 g. of hydroxylamine hydrochloride. The solution was warmed very gently for a few minutes and then placed in an ice–salt bath for one-half hour. The mannose oxime crystallized immediately upon scratching the sides of the flask with a glass rod. The crystals were filtered and washed with a little ice water; yield, 7.8 g.; m. p. 175–177°.

Mannonic Acid Nitrile Penta-acetate.—Six grams of mannose oxime was treated with 40 cc. of acetic anhydride and 6 g. of fused sodium acetate, by heating the reaction mixture to 85–90°. At this point the flask was removed from the source of heat and the reaction started with a rapid increase in temperature to the boiling point of the mixture. After the reaction was apparently over, the mixture was heated at its boiling point for one minute. It was then cooled and poured upon four times its volume of cracked ice with stirring. The sirup which separated was washed repeatedly with ice water and placed in the ice box. After four or five hours the sirup crystallized. This material had a very dark color which was removed by dissolving in boiling water and treating with norite. The water solution upon cooling gave a crop of almost white product This material was recrystallized four times from a few cubic centimeters of alcohol; yield, 2.5 g.; m. p. 92–93". This material gave a polarization value of $[\alpha]^{29}_{\mathrm{D}}$ −1.8"

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[15] E. Fischer and J. Hirschberger, *Ber.*, 22, 1155 (1889).

(0.3878 g. of subs., 10.06 cc. of U. S. P. chloroform soln., α = −0.07°, 1.0-dm. tube). After one further recrystallization the m. p. 92–93', and the polarization value $[\alpha]_D^{30}$ −1.1° (0.3525 g. of subs., 10.06 cc. of U. S. P. chloroform soln., a = −0.04°, 1.0-dm. tube), were obtained.

The substance is soluble in cold chloroform, slightly soluble in cold alcohol, insoluble in cold water, slightly soluble in hot water, very soluble in hot alcohol and insoluble in petroleum ether. It crystallizes in plates.

Anal. Subs., 0.3030: N_2, 10.3 cc. (748.2 mm., 27°). Subs., 0.1993: CO_2, 0.3617; H_2O, 0.0993. Calcd. for $C_6H_6O_5N(CH_3CO)_5$: C, 49.56; H, 5.46; N, 3.61. Found: C, 49.49; H, 5.58; N, 3.68.

Measurement of Constants of Gluconic Acid **Nitrile** Penta-acetate.—Ten grams of gluconic acid **nitrile** penta-acetate which had been recrystallized once, after three further recrystallizations from the smallest possible volume of hot alcohol, had a melting point of 82.5–84°. After three more recrystallizations its melting point was 83–84°. The polarization value of the pure substance was $[\alpha]_D^{29}$ +47.8° (0.9354 g. of subs., 24.88 cc. of U. S. P. chloroform soln., α = +1.80°, 1.0-dm. tube). A second determination gave the value $[\alpha]_D^{31}$ +48.3° (0.3505 g. of subs., 10.02 cc. of U. S. P. chloroform soln., a = +1.69°, 1.0-dm. tube). The substance crystallizes in plates.

Measurement of Constants of **β-Glucose Oxime.—We** have been able to recrystallize glucose oxime in one-gram lots from 60% methyl alcohol by boiling with 15 cc. of the solvent for not more than one-half minute, decanting the supernatant liquor, and cooling it rapidly. If the solution is kept hot too long the glucose oxime will not crystallize. After two recrystallizations in this way the material gave a melting point of 139–140°, an initial polarization value of $[\alpha]_D^{25}$ −8.9° and a final value of $[\alpha]_D^{25}$ −1.9° (1.0260 g. of subs., 25 cc. of water soln., initial a = −0.73°, final a = −0.07°, 2.0-dm. tube). A melting point of 142–143" was obtained for this substance when prepared by de-acetylation of aldehydo-glucose oxime penta-acetate. In this case an initial specific rotation of −8.3" and a final value of −3.0" were obtained.

B.—**Reactivity** of Glucose Oxime and its Acetates

De-Acetylation of Aldehydo-glucose Oxime Penta-acetate.—An attempt to de-acetylate aldehydo-glucose oxime penta-acetate in acid solution resulted in splitting the oxime linkage. The compound was successfully de-acetylated in alcoholic ammonia. Five grams of aldehydo-glucose oxime penta-acetate was dissolved in 25 cc. of methyl alcohol and dry ammonia bubbled through the solution for fifteen minutes at 0°. The solution was placed in the ice box for twenty-four hours. It was then evaporated under reduced pressure at 35° to a thick sirup, which was dissolved in 10 cc. of ethyl alcohol, nucleated with known glucose oxime and placed in an oven at 37°. Glucose oxime slowly separated out, taking several days to crystallize completely; yield, 0.85 g., m. p. 135–138°. A mixed melting point with known glucose oxime (m. p. 139°) was 135–138°. After one crystallization from 80% ethyl alcohol the melting point was 142–143" and a mixed melting point with known material was 140–141°. It gave an initial polarization value of $[\alpha]_D^{29}$ −8.3" and a final value of $[\alpha]_D^{29}$ −3.0° (0.3380 g. of subs., 10.06 cc. of water soln., initial α = −0.28°, final α = −0.10°, 1.0-dm. tube).

Aldehyde-glucose Oxime Penta-acetate.—On heating aldehydo-glucose oxime penta-acetate slowly to 200°, it began to decompose. The heating was stopped at this point and the product dissolved in hot water. Only unchanged material was isolated.

Aldehyde-glucose Oxime Hexa-acetate, **Nitrile** Formation.—Two grams of aldehydo-glucose oxime hexa-acetate (m. p. 119.5") was carefully melted and then heated to 135–140°. At this point the substance began to decompose and on removal from the source of heat the reaction continued spontaneously with a rapid rise in temperature.

After the reaction was completed, the resulting sirup was poured into cold water. It crystallized almost immediately. On one recrystallization from dilute alcohol, 1.4 g. of material melting at 82–83° was obtained. One further crystallization gave material melting at 83–84° and showing no depression when mixed with an authentic specimen of gluconic acid nitrile penta-acetate (m. p. 83–84°). It gave a polarization in chloroform of $[\alpha]^{27}_{D}$ +47.8° (0.4040 g. of subs., 10.06 cc. of U. S. P. chloroform soln., $\alpha = +1.92°$, 1-dm. tube), in exact agreement with the value determined for the nitrile acetate.

Two grams of aldehydo-glucose oxime hexa-acetate (m. p. 119.5°), 2 g. of fused sodium acetate and 8 cc. of acetic anhydride were heated at the boiling point of the mixture for ten minutes and then poured on cracked ice. The resulting sirup was washed several times with cold water, recrystallized from water and then twice from dilute alcohol. The melting point was 83–84° and showed no depression on admixture with an authentic specimen of gluconic acid nitrile penta-acetate (m. p. 83–84°). The polarization value in chloroform was $[\alpha]^{27}_{D}$ +46.8° (0.2269 g. of subs., 10.06 cc. of U. S. P. chloroform soln., $\alpha = +1.06°$ 1-dm. tube). The rotatory value previously determined for the acetylated nitrile was +47.8°.

6-Glucose Oxime Hexa-acetate.—This substance did not form gluconic acid nitrile penta-acetate when heated alone to high temperatures or with acetic anhydride and sodium acetate. The compound underwent profound decomposition when heated alone to high temperatures. If treated according to Wohl's procedure for the formation of the acetylated nitrile, the material was recovered unchanged in high yield.

β-Glucose Oxime: **Nitrile** Formation **and** Isolation **of** Intermediate Form.—Ten grams of β-glucose oxime, 10 g. of fused sodium acetate and 40 cc. of acetic anhydride were heated to a temperature of 75–80° for one hour. These conditions were identical with those used by Wohl except that the reaction was run for a longer time at a lower temperature. The solution was then poured into 200 cc. of ice water and allowed to stand overnight. The solid material from four such runs was combined, dissolved in the smallest possible volume of hot ethyl alcohol and water added to opalescence at room temperature. The material which separated was recrystallized four times from hot ethyl alcohol. It yielded 16 g. of gluconic acid nitrile penta-acetate, m. p. 83–84° and giving a polarization value of $[\alpha]^{29}_{D}$ + 47.6° (0.4227 g. of subs., 10.06 cc. of U. S. P. chloroform soln., $\alpha = +2.00°$ 1-dm. tube). The constants determined for the pure substance are m. p. 83–84°, $[\alpha]_{D}$ +47.8°. The ice water used to hydrolyze the acetic anhydride solution was extracted with chloroform, the extract evaporated and the residue crystallized by dissolving in hot ethyl alcohol and adding water to incipient opalescence. The filtered material was recrystallized from alcohol-free ether. The alcohol mother liquor from the first recrystallization of the nitrile was diluted to 400 cc. with water, extracted with chloroform and the extract treated as above. The filtered material from these two sources was combined and recrystallized four times from alcohol-free ether and finally from dilute ethyl alcohol. The yield was 0.2 g. of material, m. p. 119°. A mixed melting point with an authentic specimen of aldehyde-glucose oxime hexa-acetate (m. p. 119.5°) was 119.5°, while on admixture with β-glucose oxime hexa-acetate (m. p. 113–115°) the melting point was depressed to 103–106°. The isolated material gave a polarization value of $[\alpha]^{31}_{D}$ +45.9° (0.2150 g. of subs., 10.06 cc. of U. S. P. chloroform soln., $\alpha = +0.98°$, 1-dm. tube). The polarization value determined for the pure substance in this solvent was $[\alpha]_{D}$ +46°. Doctor V. H. Morris of the Ohio Agricultural Experiment Station has made a comparison of the optical properties of the above isolated material with those of aldehydo-glucose oxime hexa-acetate synthesized through aldehydo-glucose penta-acetate and states that "the optical constants of the two samples are identical."

The yield of 0.2 g. reported above is probably not representative of the total amount of this substance in the acetylation mixture, since its separation is difficult and most of the material is lost in purification.

β-Glucose Oxime Hexa-acetate. Isolation from **Wohl's Acetylation** Mixture.—Since Wohl[9] merely reported a melting point for the oxime acetate obtained by him and gave no directions for its isolation, it was thought advisable to repeat this work. It was also of interest in our work to determine that when the acetylation of the oxime had gone to completion, no trace of the aldehydo-oxime acetate could be found. Five grams of glucose oxime was acetylated according to Wohl's procedure and the reaction mixture poured into 300 cc. of cold water. The liquid decanted from the sirup formed was extracted with chloroform and the evaporated extract dissolved in a small quantity of ethyl alcohol. To this solution was rapidly added about four volumes of water and the solution decanted from the sirup precipitated. A crop of crystals appeared in the decanted solution. After one recrystallization from alcohol and water the melting point was 113–115° and showed no depression on admixture with an authentic specimen of β-glucose oxime hexa-acetate (m. p. 113–115°) and gave a melting point of 100–105" on mixing with aldehydo-glucose oxime hexa-acetate (m. p. 119.5")

Summary

1. The penta-acetate and hexa-acetate of the open-chain form of glucose oxime have been synthesized in pure crystalline condition.

2. Evidence is given that the ring form of glucose oxime shifts to the open-chain form on undergoing nitrile formation. This evidence is based upon the direct isolation of the intermediate open-chain oxime acetate from the reaction mixture when the reaction is stopped before completion.

3. Acetic acid and not water is split out on nitrile formation from glucose oxime.

4. The acetylated oxime isolated by Wohl and considered to be the *anti* form of glucose oxime hexa-acetate is shown to be a ring form, corresponding in structure to glucose oxime. It is shown that these ring forms are probably the beta isomers.

5. The open-chain form of glucose oxime penta-acetate yields the ring form of glucose oxime on de-acetylation.

6. A nomenclature is suggested which distinguishes between the ring forms and the open-chain forms of sugar oximes.

7. Evidence is given that glucose oxime does not react in the pseudo oxime form on undergoing nitrile formation.

8. Mannonic acid nitrile has been synthesized in pure crystalline condition.

9. Constants are given for β-glucose oxime hexa-acetate, β-glucose oxime, and gluconic acid nitrile penta-acetate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, UNIVERSITY OF NORTH CAROLINA]

THE IODINE CONTENT OF SHRIMP WASTE

BY HAYWOOD PARKER, JR.,[1] AND FRANK C. VILBRANDT[2]

RECEIVED JULY 30, 1930 PUBLISHED FEBRUARY 9, 1931

The recent investigation of Vilbrandt and Abernethy[3] on the utilization of the waste products of the shrimp fisheries has shown that a high protein stock feed, rich in vitamins, can be produced economically from the shrimp waste. Since practically all marine life contains comparatively large quantities of iodine, the above wastes from shrimp have been examined for iodine content.

Source of Material.—The shrimp waste used in this investigation was taken from the composite of a number of brine cooks prepared by Vilbrandt and Abernethy[3] during the summer of 1928 at Brunswick, Ga. The waste from the shrimp picking tables had been boiled in brine, then removed from the cooking liquor and dried to a moisture content of 4.4%. This material had been kept in this condition for twenty-two months with no indication of deterioration. The methods of Baumann,[4] Paolini[5] and McClendon[6] were used to reduce the shrimp waste to a condition whereby extraction could be accomplished efficiently.

Methods for Determining Iodine.—The analytical method used in this investigation was the Tressler and Wells[7] modification of the von Fellenberg extraction method. In the case of the extracts prepared and analyzed, one gram of the shrimp waste was used as a base to distribute and support the extract. This procedure added a definite constant amount of iodine to the extraction values; a correction was made for this iodine added.

Experimental Data.—The treatment of the shrimp waste to ascertain the distribution of the iodine was varied by using several solvents and methods of extraction. The extraction data and the iodine content of the various extracts are given in Table I.

Of the various treatments used, simple extraction with ethyl alcohol, water and ethyl ether, in the order named, gave the most efficient separation of iodine. The ether extract contained the lipoid iodine, while the water and alcohol extracts contained considerable quantities of organically combined iodine as well as the inorganic iodine.

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[2] Department of Chemical Engineering, Iowa State College, Ames, Iowa.

[3] F. C. Vilbrandt and R. F. Abernethy, "Utilization of Waste Shrimp," U. S. Bur. of Fisheries, Doc. 1078 (1930).

[4] Baumann, *Z. physiol. Chem.*, 21, 319–330 (1895–1896).

[5] N. Paolini, *Inst. Chim. Pharm., Rome Univ. Mon. Sci.*, 23, 648 (1894).

[6] McClendon and others, THIS JOURNAL, 52,541 (1930).

[7] O. K. Tressler and A. W. Wells, "Iodine Content of Sea Foods," U. S. Bur. of Fisheries, Doc. 967.

TABLE I

IODINE CONTENT OF EXTRACTS OF SHRIMP WASTE

Treatment	Solvent	Concn., %	Sample, g.	Nature of residue	Iodine in sample, P. P. m. Sol.	Insol.	Total	Iodine, % Sol.	Insol.	Iodine found, %
1	...	...	..	....	..	...	16.90	..	...	100.0
2	Alcohol	96	30	Brown tar	4.68	2.78	7.46	62.7	37.3	44.1
3	Ether	100	30	Greenish brown oil	3.45	5.95	9.40	36.7	63.3	55.6
4	Water	...	60	Brown tar	9.15	7.65	16.80	54.5	45.5	99.4
5	HCl	5	30	Putrid brown mass	..	10.10	10.10	0.0	100.0	60.0
6	NaOH	5	30	Putrid brown mass	8.00	8.94	16.94	47.2	52.8	100.0

The results of the acid hydrolysis indicated that coagulation of protein matter caused by the acid tended to render the iodine compounds insoluble. The alkaline hydrolysis showed that a large fraction of the iodine is held in some organic combination, probably protein, quite resistant to decomposition. It will be noticed that the values for total iodine, obtained by adding the extract iodine and residue iodine, are low in the samples treated with alcohol and with ether. It is possible that some of the loss of iodine is due to volatilization of some organic iodides, possibly ethyl iodide formed with the alcohol itself or the alcohol present in the ether.

These experiments show that the shrimp waste contains a relatively large proportion of iodine. The majority of this iodine is held in organic combination, 26.7% being combined with the lipoid material, and the rest probably occurring in protein combination.

Examination for Thyroxine.—An attempt was made to isolate thyroxine from the shrimp waste by means of Kendall's[8] method of hydrolysis, modified slightly in the extraction procedure due to the peculiar nature of the waste. Upon proper extraction the Kendall precipitate, which should normally contain the thyroxine if any were present, was so small that it was deemed inadvisable to make a direct iodine determination; instead, the substance in solution, slightly yellow in color, was tested for the presence of thyroxine according to the nitrous acid method cited by Kendall,[8] with negative results. The addition of ammonium hydroxide to the resultant solution also produced no color change, thus indicating that thyroxine could not be detected in the extract of shrimp waste by the Kendall method.

Summary

1. The wastes of shrimp fisheries showed a content of **16.9** parts per million of iodine calculated on the dry basis.
2. Alcohol extraction indicated the presence of **44.14%** of organic plus inorganic iodine.

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[8] E. C. Kendall, Thyroxine, American Chemical Society Monograph Series, No. 47.

3. Ether extraction indicated the presence of 55.86% of lipoid iodine.

4. No thyroxine could be detected in the extract of shrimp waste when tested by the Kendall method.

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THE REDUCING ACTION AND CONSTITUTION OF THE GRIGNARD REAGENT

BY C. R. NOLLER

RECEIVED SEPTEMBER 10, 1930 PUBLISHED FEBRUARY 9, 1931

A. Reducing Action

The occurrence in the literature of over fifty references to the reduction of various compounds, chiefly aldehydes, ketones and esters, brought about by Grignard reagents indicates the frequency with which this side reaction is encountered. During the past year alone, from papers and a note have appeared dealing primarily with this subject.[1]

An examination of the various experiments leads one to the conclusion that the reduction may be due to a number of causes. It may be brought about by the action of unused magnesium and the magnesium halide which is always present,[2] by the action of magnesium alcoholate on an excess of the aldehyde or ketone,' or by the action of the Grignard reagent itself. It would seem that, strictly speaking, only the last type of reduction should be considered as the reducing action of the Grignard reagent, but even in this case reduction may be brought about in at least two ways. Where dissociation of the Grignard reagent into the free hydrocarbon radical and magnesious halide may take place, the latter may cause reduction.*

In other cases reduction takes place at the expense of the hydrocarbon radical with the formation of unsaturated hydrocarbon.[5] It should be

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[1] (a) Hatt, *J. Chem. Soc.*, 1623 (1929); (b) Conant and Blatt, THIS JOURNAL, 51,1227 (1929); (c) Blicke and Powers, *ibid.*, 51,3378 (1929); (d) Grignard and Delarue, *Bull. soc. chim.*, [4] 47, 237 (1930); (e) Davies, Dixon and Jones, *J. Chem. Soc.*, 1916 (1930).

[2] Boyd and Hatt, *ibid.*, 131, 898 (1927) and Ref. 1a; Lagrave, *Ann. chim.*, [10] 8,369 (1927). See also Gomberg and Bachmann, THIS JOURNAL, 49,236 (1927).

[3] Marshall, *J. Chem. Soc.*, 105, 527 (1914); 107, 509 (1915); 127, 2184 (1925); Meisenheimer, *Ann.*, 446, 76 (1926).

[4] Gilman and Fothergill, THIS JOURNAL, 51,3149 (1929).

[5] Of the several theories that have been proposed for this last type of reduction, the assumptions (1) that after a primary addition of RMgX to the aldehyde or ketone, unsaturated hydrocarbon is lost and the remaining HMgX adds to the carbonyl group [Hess and Rheinboldt, *Ber.*, 54,2043 (1921); Hess and Wustrow, *Ann.*, 437, 256 (1924); Rheinboldt and Roleff, *Ber.*, 57, 1921 (1924); Meisenheimer, *Ann.*, 442, 180 (1925); Rheinboldt and Roleff, *J. prakt. Chem.*, 109, 175 (1925)] and (2) that the free radicals RR'C(OMgX)— and R''— are intermediate products in the reaction of a ketone RCOR'

noted that the products of these various types of reduction are not the same. Magnesium halide or magnesium and magnesium halide seem to lead to the formation of pinacols, whereas magnesium alcoholate and undissociated Grignard reagent yield alcohols.[5,6]

With the appearance of the excellent work of Schlenk and Schlenk[7] on the composition of the Grignard reagent in which direct evidence was advanced for the equilibrium

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (1)$$

it seemed desirable to determine whether solutions of R_2Mg alone would cause reduction. In choosing a reaction for study it was thought advisable to use one that normally caused a very large amount of reduction. The reaction of isobutylmagnesium iodide and benzophenone reported by Blicke[1c] to give a 74% yield of benzhydrol satisfied this condition, and the ease with which the reduction product was isolated seemed to be an added advantage. Isobutyl bromide was used in place of isobutyl iodide because it is more readily prepared and probably rearranges to the tertiary halide less readily.

Schlenk's method[7] was used for preparing solutions of di-isobutyl magnesium. It was found that the equilibrium *(1)* is shifted so far to the right in the Grignard reagent prepared from isobutyl bromide that approximately 75% of the active Grignard reagent is present in the form of di-isobutyl magnesium. Precipitation of the halogen-containing compounds with 1,4-dioxane therefore gave a ready means of obtaining fairly concentrated solutions of di-isobutyl magnesium (0.1–0.14 equivalent or 0.05–0.07 mole per 100 cc. of solution). These solutions could be prepared containing less than 0.1 equivalent per cent. of the active Grignard reagent combined with halogen, as determined by analysis for halogen.[8] In all of

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with $R''MgX$ (Biicke, Ref. 1c) seem to be the most satisfactory. The latter theory, however, leads one to predict the formation of pinacols in the absence of excess of magnesium. Until recently, the only case where this occurred was with triphenylmethylmagnesium chloride.[4] Recently, Davies, Dixon and Jones[10] report the isolation of benzpinacol from the reaction of amylmagnesium halides with benzophenone. Unfortunately. they siphoned or decanted their solutions from the excess magnesium. That this may not be sufficient is shown by the experiments of Gilman and Fothergill (Ref. 4, note g) with *tert.*-butylmagnesium chloride. Since the appearance of the work of Davies, Dixon and Jones, we have re-examined 60 g. of the combined solid fractions obtained in the reaction of isobutylmagnesium bromide and benzophenone and have been unable to find any indication of the presence of benzpinacol.

[6] An entirely different type of reduction seems to take place in the action of Grignard reagents on azobenzene [Rheinboldt and Kirbig, *J. prakt. Chem.*, [2] 118, 1 (1928)] and in the reaction of certain bromides with magnesium [Krestinsky, Ber., 55, 2770 (1922)].

[7] Schlenk and Schlenk, *ibid.*, 62, 920 (1929); see also Gilman and Fothergill, Ref. 4.

[8] One of the referees has pointed out that a small amount of MgX_2 because of the equilibria involved might suffice to convert a large amount of R_2Mg to $RMgX$. We do

the work reported in this paper, perfectly clear filtered solutions of the Grignard reagent were used and always in 10% excess.

We have found that solutions of di-isobutyl magnesium reduce benzophenone to benzhydrol to the extent of at least 64% of the theoretical amount. The high percentage of di-isobutyl magnesium present in the original Grignard solution (approximately the same as the amount of reduction reported by Blicke) seemed to indicate that it was the sole reducing agent. However, when benzophenone in benzene solution is added to the original Grignard reagent, a copious precipitate is soon formed from which the reduction product is isolated; when added to a solution of di-isobutyl magnesium, no precipitate is formed and the reduction product is obtained on decomposing the solution and crystallizing the benzhydrol from the other reaction products. On comparing the relative amounts of benzhydrol isolated in each case, it would appear that more reduction takes place when the original Grignard reagent is used (83.5%) than when a solution of di-isobutyl magnesium is used (64.2%). Because of the greater difficulty in isolating the benzhydrol in the second case, however, the amount formed is undoubtedly larger than was actually isolated. Whether or not the amount of reduction was identical, it was certainly greater than 64% in both cases.

Blicke assumed the precipitate from which the benzhydrol was isolated in the first case to have the formula $(C_6H_5)_2CHOMgBr$, having shown that a similar precipitate is formed on adding a solution of benzhydrol to the Grignard reagent prepared from ethyl bromide. No analyses were given. We have determined the ratio of the benzhydrol to the basic hydroxyl groups and to the halogen after the precipitate is decomposed with water, and find that it agrees with this formula. It would appear therefore that solutions containing only di-isobutyl magnesium can cause reduction of benzophenone to the extent of at least 64%, the reduction product probably existing in the form $(C_6H_5)_2CHOMgOCH(C_6H_5)_2$, which is soluble in ether. When, on the other hand, the original Grignard reagent is used, only isobutylmagnesium bromide causes reduction, the reduction product precipitating entirely in the form $(C_6H_5)_2CHOMgBr$, and this in spite of the fact that 75% of the active Grignard reagent is in the form of di-isobutyl magnesium.

B. Constitution of the Grignard Reagent

In order that reduction may be brought about entirely by means of isobutylmagnesium bromide, the equilibrium (1) must shift very rapidly,

not feel that this is likely, however, because Gomberg and Bachmann (Ref. *2)* and more recently Bachmann [THIS JOURNAL, 52,4412 (1930)] find that in reactions depending on similar equilibria the rate is slower when only a small amount of MgX_2 is present than when an equivalent quantity of MgX_2 is present, whereas in our experiments reaction always takes place very rapidly. The suggestion is, nevertheless, one to be kept in mind since the rates of attaining equilibrium may be vastly different in different reactions.

because so far as one can tell by the evolution of heat and immediate precipitation of the reduction product (after precipitation once starts), the reduction is practically instantaneous. This would not be a serious drawback, however, because Schlenk[7] has shown that although the equilibrium in the case of ethylmagnesium iodide is only slowly attained, the equilibrium in the case of phenylmagnesium bromide must be reached quite rapidly. The reduction of benzophenone by di-isobutyl magnesium, however, must also, as evidenced by the evolution of heat, be practically instantaneous. It is difficult to see, therefore, why the original Grignard reagent which is in the form of di-isobutyl magnesium to the extent of 75% should shift entirely to the form isobutylmagnesium bromide during the reduction when either compound may cause reduction.

At this point it occurred to us to determine what would happen if a solution of anhydrous magnesium bromide in absolute ether were added to the solution containing the reduction product formed by the action of di-isobutyl magnesium. It was found that a compound is rapidly precipitated (again after precipitation once starts) which so far as can be determined from analysis, appearance and behavior is identical with that formed when benzophenone is added to the original Grignard reagent. This would mean, assuming Blicke's formula to be correct, that the reaction

$$(C_6H_5)_2CHOMgOCH(C_6H_5)_2 + MgBr_2 \rightleftharpoons 2(C_6H_5)_2CHOMgBr \qquad (2)$$

is likewise a very rapid one.

Considerable work has been done in attempts to decide between the formulas RMgX and $R_2Mg{\cdot}MgX_2$ for the Grignard reagent.[9] The majority of this work seems to favor the RMgX formula, but with the possible exception of the results of Job and Dubien[10] on the order of the reaction

$$C_2H_5MgBr + C_2H_5Br \rightleftharpoons C_2H_4 + C_2H_6 + MgBr_2 \qquad (3)$$

of which no experimental details are given, the writer does not believe that any of the work gives conclusive evidence for either formula. Until such evidence is presented, it would appear that the reactions discussed in this paper are best explained by assuming that no isobutylmagnesium bromide exists in the original Grignard solution, that the equilibrium existing in this solution is best represented as

$$R_2Mg{\cdot}MgX_2 \rightleftharpoons R_2Mg + MgX_2 \qquad (4)$$

and that the insoluble compound has the composition $[(C_6H_5)_2CH{-}O]_2$-$Mg{\cdot}MgBr_2$, where the dots simply represent some form of molecular complex. Such reactions involving the formation of simple addition products would be expected to take place more rapidly than metathetical

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[9] For references to this work see Note **3** in the paper by Gilman and Fothergill **(Ref.** 4).

[10] Job and Dubien. Bull *soc chim.*, **[4] 39, 583** (1926); *Compt. rend.*, **184,** 155 **(1927).**

reactions in a slightly ionizing solvent such as anhydrous ether, **and a** single compound, the dialkyl magnesium, would be responsible for reduction.

Experimental

Isobutyl Bromide.—Isobutyl alcohol, b. p. 106–107.5°, was mixed with a 50% excess of constant-boiling hydrobromic acid and the mixture slowly distilled through a 1-m. column until the temperature reached 120°. The distillate was saturated with salt, the bromide layer separated, returned to the flask containing the residue of hydrobromic acid and distilled again. This operation was repeated until the bromide layer had a specific gravity of approximately 1.2. It was then washed twice with concd. sulfuric acid, once with 5% sodium carbonate solution, then with water and dried over calcium chloride. This product was carefully fractionated three times through a 1-m. column, the main portion boiling at 91–93'. Analysis according to the method of Michael[11] showed 5.1% of tertiary butyl bromide. After vigorously stirring this product for thirty minutes at 25° with fifty times its weight of water, drying over anhydrous potassium carbonate, and distilling, analysis showed 0.96% tertiary butyl bromide.

Grignard Reagent.—The entire preparation and filtering operations were carried out in an atmosphere of hydrogen. About 10 cc. of a mixture of 137 g. (1 mole) of isobutyl bromide and 150 cc. of absolute ether was added to 24.5 g. of fine, bright magnesium turnings in a one-liter three-necked flask fitted with condenser, stirrer and dropping funnel. The reaction started almost immediately without the addition of iodine and 100 cc. of absolute ether was rapidly added. The balance of the bromide–ether mixture was then added slowly from the separatory funnel with stirring over *a* period of three hours. During this time the solution was under hydrogen at a pressure only slightly greater than atmospheric. Another 100 cc. of ether was added and the solution filtered under hydrogen pressure into a graduated cylinder and diluted to a total volume of 590 cc. The apparatus was so arranged that the solution could be transferred from the three-necked flask to a Biichner funnel with slight hydrogen pressure, filtered under a pressure of 10 pounds into the graduated cylinder, diluted to the desired volume and transferred from the graduated cylinder to a measuring buret entirely in the absence of air. The Biichner funnel had a Jena glass filter disk of porosity 3 and a 3-mm. layer of tightly packed ignited kieselguhr was used as a filtering medium.

The filtered solution was perfectly clear but still had the pale brownish-gray color characteristic of Grignard reagents. Analysis of 5-cc. portions by titration[12] with standard 0.2 N acid showed 0.001325 mole per cubic centimeter of solution. This corresponds to a total yield of Grignard reagent of 78.2%. (The actual yield of Grignard reagent, as determined in other runs in which the filtration was omitted and hence losses avoided, was approximately 86%)

Analysis **of** the Grignard Solution for Di-isobutyl **Magnesium.**—A *3G3* Jena-Biichner funnel with sintered glass filter disk was fitted through a cork with a 60-cc. glass-stoppered separatory funnel and a stopcock for applying hydrogen pressure. The apparatus was swept out with hydrogen, 5 cc. of absolute ether run into the funnel to moisten the glass filtering disk (no other filtering medium was used) and 5 cc. of the Grignard reagent run into the separatory funnel from a buret. To this was quickly added 1.5 cc. of a solution of pure 1,4-dioxane in absolute ether (1 g. per 2 cc. of solution). The separatory funnel was closed with a well-greased stopper and shaken. The mixture was then run into the Biichner funnel and filtered with hydrogen pressure. The sepa-

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[11] Michael, *Ann.*, **379, 287** (1911).

[12] Gilman and co-workers, THIS JOURNAL, 45, 150 (1923); 51, 1576 (1929).

ratory funnel and precipitate were washed three times with 5-cc. portions of ether, filtering each time with pressure. The filtrate was decomposed with 50 cc. of water, the ether removed by heating on a hot-plate, and the magnesium hydroxide titrated with standard acid.[13] The average amount of acid, calculated *as* 1 N, was 4.967 cc., indicating that approximately 75% of the active Grignard solution was in the form of di-isobutyl magnesium.

Preparation of Di-isobutyl Magnesium Solution.—Three hundred cubic centimeters of the Grignard reagent from isobutyl bromide was placed in a 500-cc. glass-stoppered flask previously swept out with hydrogen, and cooled in an ice–salt bath to 0°. To this was added with shaking 66 cc. of a solution of dioxane in ether (50 g. per 100 cc.). The temperature did not rise above 20°. After thorough shaking the mixture was poured into four 100-cc. centrifuge tubes and tightly stoppered. After centrifuging for fifteen minutes at about 2000 r. p. m., a clear upper layer had formed. This still gave a slight precipitate with dioxane solution and a total of 7 cc. more was added to each tube, when practically no more precipitate formed. The tubes were again centrifuged and then decanted into a hydrogen filled bottle. This solution is perfectly clear and water white, being entirely free from the grayish color of the original Grignard solution. The concentration of active Grignard reagent as determined by titration with standard acid was 0.00101 equivalent per cubic centimeter. The solution gave a weak test for halogen. To 10 cc. of the solution was added 100 cc. of water and then 10 cc. of 6 N nitric acid. This solution was titrated with an approximately 0.1 N standard silver nitrate solution. An amount equivalent to 0.0079 cc. of N silver nitrate was required, indicating 0.078% of the Grignard reagent combined with halogen.

Reducing Action of the Original Grignard Solution.—In an Erlenmeyer flask fitted with a thermometer and a 50-cc. dropping funnel was placed 41.5 cc. (0.055 equiv.) of the Grignard solution and this diluted with 13.5 cc. of absolute ether to make the equivalent concentration of active Grignard reagent the same as that of the di-isobutyl magnesium solution prepared above. The flask was placed in an ice–salt mixture and when the temperature had dropped to 0°, a solution of 9.1 g. (0.05 mole) of benzophenone dissolved in 10 cc. of dry benzene was slowly added, shaking after each addition. The rate of addition was such that the temperature was kept between 0 and 5°. With the addition of each drop of benzophenone solution, a deep wine red color was imparted to the solution, which soon disappeared. After a short time a white precipitate began to form which settled out very readily. The formation of a red color each time the solution of benzophenone was added took place at the end of the reaction just as at the beginning. The mixture was allowed to warm up to room temperature and then filtered on a Büchner funnel with suction, washing the precipitate three times with 10-cc. portions of dry benzene. The filtrate and precipitate were decomposed separately with a saturated solution of ammonium chloride and extracted three times with 50-cc. portions of ether. The ether solutions were evaporated in a tared beaker placed on a watch glass, at first over a warm hot-plate and finally in a vacuum desiccator over phosphorus pentoxide.[14] There was obtained from the precipitate 7.7 g. of benzhydrol melting at 65–67° or 83.5% of the calculated amount. The filtrate yielded 1.3 g. of an oil from which nothing could be crystallized. Assuming this to be diphenyl isobutyl carbinol, it would correspond to 10.8%, making the total recovery 94.3%.

Reducing Action of Di-isobutyl Magnesium Solutions.—The procedure followed

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[13] Whenever an appreciable amount of ether is present it is necessary to remove it in order to get a satisfactory end-point with phenolphthalein. This is in agreement with the work of Hall [*Ind. Eng. Chem., Anal. Ed.*, 2, 244 (1930)] on the analysis of ether.

[14] Excessive heating must be avoided to prevent the formation of dibenzhydryl ether which seems to take place at times even at temperatures near 100°.

was the same as in the previous experiment, using 110 cc. (0.11 equiv.) of di-isobutyl magnesium solution and 18.2 g. (0.10 mole) of benzophenone in 20 cc. of dry benzene. As in the preceding experiment, a deep red color developed after each addition of benzophenone, which soon disappeared on shaking. This reaction differed from the preceding one, however, in that no precipitate formed. After all of the benzophenone had been added, the solution was allowed to warm up to room temperature and a clear pale yellow solution resulted. The entire solution was decomposed with a saturated ammonium chloride solution, extracted three times with 50-cc. portions of ether, and the ether and benzene removed as before. There was obtained 18.5 g. of an oil which partially solidified on standing. Filtration was rather difficult so the whole was dissolved in 10 cc. of 95% alcohol, cooled until crystallization was complete, and filtered with suction. The filtrate was cooled again in an ice–salt mixture and filtered. A total of 10.4 g., m. p. 59–64°, was obtained. The combined alcoholic solution, including alcoholic washings of funnel, beakers and filter papers, was evaporated at 25 mm. and finally heated at 100° for ten minutes at this pressure. After standing for several days crystals appeared and on stirring a paste of crystals resulted. On filtering, oily crystals were obtained which weighed 1.4 g. and after clay plating melted at 59–65°, making the total recovery of benzhydrol 11.8 g. or 64.2% of the calculated amount. The total amount of oil remaining was 3.8 g., so that a loss of 2.9 g. occurred. The difference between the original weight and the weight of benzhydrol is 6.7 g. Assuming this to be diphenyl isobutyl carbinol it amounts to 27.9% of the calculated amount, making the total yield of products 92.1%. The actual amount of benzhydrol formed must be considerably greater than was actually isolated.

Analysis of Precipitate Formed on **Adding** Benzophenone to the Original Grignard Reagent.—A Grignard solution was prepared as previously described except that one-third quantities were used and the final solution was less dilute. Analysis by titration with standard acid showed it to contain 0.001927 equivalent of active Grignard reagent per cubic centimeter. Two 20-cc. (0.0385 equiv.) portions of this solution were treated with solutions of 6.3 g. (0.0347 mole) of benzophenone in 10 cc. of dry benzene. The precipitates were centrifuged, the clear liquid decanted and the precipitate washed four times with 30-cc. portions of *dry* benzene, stirring the precipitate and centrifuging each time. After the last centrifuging the tube was swirled so as to remove an upper gelatinous layer with the benzene when the latter was decanted. No attempt was made to obtain all of the precipitate, the sole object being to get a pure product. Ether was added to the precipitate to facilitate removal and the whole transferred to an Erlenmeyer flask, where it was decomposed with 100 cc. of distilled water. The solutions were extracted four times with 50-cc. portions of alcohol-free ether and the ether evaporated from the solution in a tared beaker, at first over a warm hot-plate and finally in a vacuum desiccator over phosphorus pentoxide.

The aqueous layers were boiled to remove ether and after cooling titrated with approximately 0.5 N standard nitric acid. These same solutions were then diluted to 500-cc. and 50-cc. portions acidified with nitric acid and titrated with approximately 0.1 *N* standard silver nitrate solution. The results are given in Table I.

TABLE I

ANALYSIS OR PRECIPITATE FROM ORIGINAL GRIGNARD REAGENT AND BENZOPHENONE

Sample	G.	Benzhydrol equiv.	M. p., °C.	*N* HNO_3, cc.	Equiv. of basic OH	*N* $AgNO_3$, cc.	Equiv. of halogen
1	4.28	0.0233	66–67.5	23.02	0.0230	23.20	0.0232
2	4.17	.0227	67.5–68	22.80	.0228	22.81	.0228

These results show that on decomposing the precipitate with water there is obtained one equivalent of benzhydrol for one equivalent each of basic hydroxyl and halogen.

Analysis of the Precipitates Formed on Adding a Solution of Anhydrous Magnesium Bromide to a Solution of the Reaction Product of Benzophenone and Di-isobutyl Magnesium.—Anhydrous magnesium bromide was prepared according to the method of Lerch.[15] On allowing the powdered fused salt to stand for several hours under absolute ether with occasional shaking, a lower yellow layer formed which according to Menschutkin[16] contains around 40% of magnesium bromide at room temperature. By dissolving **35** cc. of this lower layer in a mixture of 45 cc. of dry benzene and 30 cc. of absolute ether, a solution was obtained which could be diluted with a considerable quantity of ether without causing the separation of two layers, and a clear solution resulted when small amounts were mixed with a large volume of ether. Analysis for halogen showed it to contain 0.00089 mole of magnesium bromide per cubic centimeter.

When this solution was added to a solution of the product of the reaction of benzophenone and di-isobutyl magnesium prepared as above, an immediate precipitate was formed. On carrying out a fractional precipitation and analyzing the precipitates, it was found that the first precipitate after decomposition with water gave practically no benzhydrol or basic hydroxyl but a large amount of halogen. The second precipitate gave a considerable quantity of benzhydrol (0.0082 equiv.) and a practically equal amount of basic hydroxyl (0.0098 equiv.) but a somewhat higher amount of halogen (0.0147 equiv.). This indicated that an excess of dioxane had been present in the di-isobutyl magnesium solution.

A solution of di-isobutyl magnesium was then prepared using a smaller excess of dioxane. To 100 cc. of the Grignard solution containing 0.001927 equivalent of active Grignard reagent per cubic centimeter was added 20 g. of dioxane dissolved in 20 cc. of ether. After centrifuging, the clear solution still gave a slight precipitate when more dioxane was added. Analysis for active Grignard reagent showed 0.00141 equivalent per cubic centimeter and for halogen 0.0000198 equivalent per cubic centimeter or 1.4 equivalent per cent.

To 65 cc. (0.092 equiv.) of this solution was added 15 g. (0.082 mole) of benzophenone dissolved in 25 cc. of dry benzene under the conditions previously given. A clear pale yellow solution resulted. This solution should require 51.5 cc. of the solution of anhydrous magnesium bromide prepared above to give an amount equivalent to the active Grignard reagent present in the di-isobutyl magnesium solution. On adding a small amount of the magnesium bromide solution, no precipitate formed, indicating that no excess dioxane was present. On adding 30 cc. of the anhydrous magnesium bromide solution, a heavy precipitate formed. The total mixture was divided into two parts and centrifuged. The clear liquids were decanted and combined and a second 10 cc. of magnesium bromide solution was added. The precipitate was centrifuged and another 10-cc. portion of magnesium bromide solution added. Only a small precipitate formed

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[15] Lerch, *J. prakt. Chem.*, [2] 28,338 (1883).

[16] Menschutkin, *Z. anorg. Chem.*, 49,207 (1906).

this time and it was entirely different in appearance from the previous precipitates in that it was yellow and gelatinous rather than white and crystalline. A final addition of magnesium bromide solution gave no further precipitate. The various precipitates were each washed four times with 20-cc. portions of a mixture of 150 cc. of dry benzene and 100 cc. of dry ether. All washings were discarded and any gelatinous layer on top of the crystalline precipitates was removed and discarded. The precipitates were then analyzed as before. The results are given in Table II.

Table II

Analysis of Precipitates from Magnesium Bromide and the Reaction Product of Benzophenone and Di-isobutyl Magnesium

Precipitate	Benzhydrol G.	Benzhydrol equiv.	Benzhydrol M. p.	*N* HNO_3, *cc.*	Equiv. of *basic OH*	*N* $AgNO_3$, *cc.*	*Equiv.* of *halogen*
1—Part A	Lost	....	.....	15.62	0.0156	15.85	0.0158
1—Part B	3.47	0.0189	65–66.5	18.56	.0186	18.69	.0187
2	2.62	.0142	62–66.5	14.04	.0140	14.13	.0141
3	0.01	.00005	.....	1.469	.0015	3.20	.0032

The main portion of the precipitate, therefore, gives analytical results identical with the precipitate formed from the original Grignard reagent and benzophenone.

Summary

1. Solutions of di-isobutyl magnesium which are practically halogen free have been shown to reduce benzophenone to benzhydrol, as well as the original Grignard reagent containing halogen.

2. The Grignard reagent prepared from isobutyl bromide at a concentration of about 1.3 molar exists to the extent of 75% in the form of di-isobutyl magnesium.

3. When the original Grignard reagent is used to reduce benzophenone, the reduction product precipitates as a white crystalline compound which yields, on decomposition with water, one mole of benzhydrol, one equivalent of basic hydroxyl, and one equivalent of halogen. When a solution of di-isobutyl magnesium is used, the reduction product remains in solution presumably in the form $[(C_6H_5)_2CHO]_2Mg$, but which can be precipitated by the addition of a solution of anhydrous magnesium bromide to give *a* compound identical by analysis with that obtained from the original Grignard solution.

4. It is believed that the constitution of the Grignard reagent represented by the equilibrium

$$R_2Mg{\cdot}MgX_2 \rightleftharpoons R_2Mg + MgX_2$$

best fits these facts and that the ether-insoluble benzhydryl magnesium salt has the composition $[(C_6H_5)_2CHO]_2Mg{\cdot}MgBr_2$.

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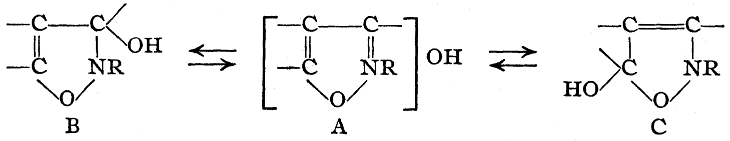
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PSEUDO BASES IN THE ISOXAZOLE SERIES. FOURTH PAPER

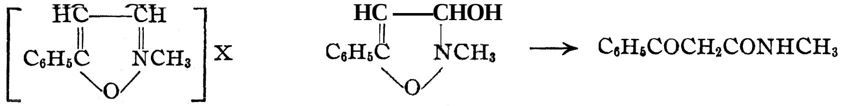
BY E. P. KOHLER AND W. F. BRUCE

RECEIVED SEPTEMBER 18, 1930 PUBLISHED FEBRUARY 9, 1931

In earlier papers of this series it has been shown that when the salts which are obtained by alkylating various isoxazoles are treated with bases they give rise to a great variety of products. All these products can be traced to two fundamental reactions which differ in the positions assumed by the hydroxyl group in the rearrangement from the true to the pseudo bases

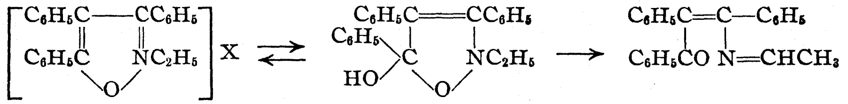


The rearrangement from **A** to B, in which the hydroxyl group ends in the 3-position, has heretofore been observed only when both the **3**- and the 4-positions were occupied by hydrogen alone, as, for example[1]



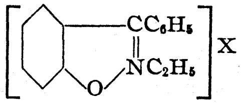
Salt *Pseudo* base *Acid amide*

In all other cases the hydroxyl group entered the 5-position and the sequence of reactions was as follows



Salt *Pseudo base* Anhydro *compound*

Before concluding our studies in this series it was desirable to investigate a case in which the **3**- and 4-positions are occupied by hydrocarbon residues but in which there is also a pronounced hindrance to the shift of linkage that is essential to a rearrangement from **A** into C. To this end we have alkylated 3-phenyl benzisoxazole and studied the behavior of the resulting salts



Except in their solubilities these salts differ but little from those obtained by ethylating triphenyl isoxazole. Even their behavior toward bases bears a certain superficial resemblance to that of the monocyclic salts, be-

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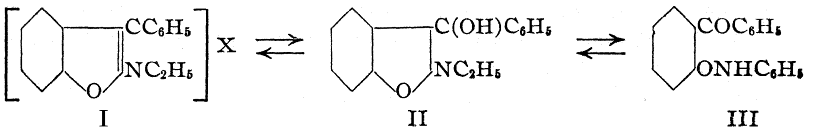
[1] Mumm and Münchmeyer, *Ber.*, *43*, 3340 (1910).

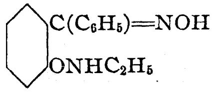
cause like these they yield, first, a pseudo base from which they can be regenerated, and finally an anhydro compound from which they cannot. Here, however, the resemblance ceases.

The pseudo base from the dicyclic salts reacts readily both with hydroxylamine and with phenyl isocyanate; it therefore behaves like an open-chained compound containing an active hydrogen atom and a carbonyl group. Such a substance manifestly can be formed only by a rearrangement of the type $A \rightarrow B$, and the relations must be represented as follows

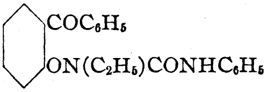


I II III

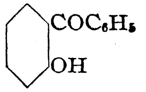
In acid solutions all transformations are toward the left, in alkaline solution they are toward the right; hence the ease with which the salts are regenerated and the inability to secure a methyl ether of II in the usual manner; hence also the ability to react with hydroxylamine and phenyl isocyanate and the readiness with which the pseudo base is oxidized to *o*-hydroxy benzophenone



IV



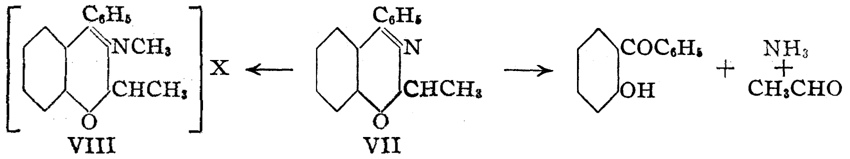
V



VI

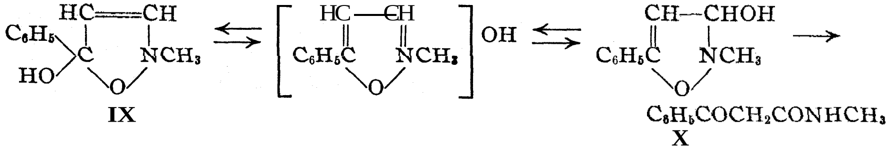
The formation of this open-chained pseudo base shows that when the hindrance to every other type of rearrangement is sufficiently great, isoxazolinium bases may rearrange to form 3-hydroxy isoxazolines even though the 3-position is occupied by a hydrocarbon residue and the lack of hydrogen in the 4-position prevents the usual adjustment to a stable acid amide. The open-chained formula, however, gives no clue to the structure of the anhydro compound. The pseudo base loses water rapidly when heated, and it even slowly passes into the anhydro compound when it is left to itself at the ordinary temperature. Despite the ease with which the process occurs, however, it must nevertheless represent a major change in structure because it cannot be reversed.

For determining the structure of the anhydro compound the following facts are available. The substance is a base, capable of forming salts that are isomeric with those derived from the pseudo base. It combines with dimethyl sulfate to form a salt in which one methyl group is in combination with nitrogen. And, finally, the anhydro compound is hydrolyzed, both by acids and by bases, to o-hydroxy benzophenone, acetaldehyde and ammonia. When these facts are assembled they lead to the metoxazine derivative VII



Doubtless there are a number of ways in which the metoxazine derivative might be formed from.the pseudo base, but whatever the route, its formation demonstrates anew the instability of all pseudo bases in the isoxazole series. In view of this great instability, it seems doubtful whether these bases can serve the main purpose of this series of investigations, namely, to ascertain the factors which determine the mode of addition of an ion to the unsaturated nucleus.

As a result of the investigations, it is now possible to predict the outcome of a reaction between a base and any isoxazolinium salt which has no substituents other than hydrocarbon residues; but in nearly all cases, there is a measure of uncertainty about the structure of the intermediate pseudo bases. In most cases the structure, of necessity, is inferred from the nature of the products into which the pseudo bases pass by spontaneous rearrangement or degradation. Since the base and the pseudo base are connected by a reversible process, inferences drawn from subsequent products are not necessarily reliable, and the fact that the final products always represent the most stable substances that could be formed leads to a suspicion that the outcome of these reactions may depend more upon the stability of the final products than upon the mode of addition. Thus the pseudo base obtained from the alkylation product of 5-phenyl isoxazole might have the structure represented by formula IX even though the final product can be reconciled only with X.



Experimental Part

Phenyl benzisoxazole was prepared as usual by converting *o*-chlorobenzophenone into its oxime and heating the oxime with bases, but it was found advantageous to combine the two steps into a single operation. The procedure was as follows.

A solution of 290 g. of hydroxylamine hydrochloride in 100 cc. of warm water was poured into a mixture of 350 g. of o-chlorobenzophenone and 300 cc. of alcohol contained in a two-liter flask. The flask was then connected with an inverted condenser and through the condenser a solution of 280 g. of sodium hydroxide in 300 cc. of water was added as rapidly as the refluxing permitted. The flask was heated for seven hours on a steam-bath and then most of the alcohol was removed by distillation. To the residue in the **flask was** added a solution of 220 g. of potassium hydroxide in 500 cc. of water.

The mixture was heated on a steam-bath for three days, then cooled to about 6° and shaken vigorously. It deposited a pale yellow solid which was thoroughly washed with water and recrystallized from methyl alcohol. It gave **220** g. of phenyl benzisoxazole, pure white in color, and melting at 81–82°—a yield of 70%.

Ethylation.—The isoxazole is ethylated less readily than those which have been studied heretofore. **A** mixture of **30** g. of the substance and **33** g of freshly distilled diethyl sulfate was heated in an oil-bath at 130–140°. The liquid darkened somewhat and there was a slow evolution of sulfur dioxide. After it had been heated for fifteen hours the mixture was cooled, treated with **50** cc. of **6** N hydrochloric acid and heated on a steam-bath for two hours. On cooling it deposited. **5** g. of unchanged isoxazole and a little more was obtained when the solution was thoroughly extracted with ether.

For the purpose of preparing the ferric chloride double salt the sirupy aqueous solution was treated with concentrated ferric chloride solution in excess. After two hours the light yellow precipitate was collected on a filter, washed with dilute hydrochloric acid and with ether, then recrystallized from **60–70** cc. of glacial acetic acid. The yield was 47 g. or 87%.

Anal. Calcd. for $C_{15}H_{14}ONCl_4Fe$: C, **42.7;** H, **3.4.** Found: C, **42.7;** H, **3.3.**

The ferric chloride double salt is readily soluble in water, very sparingly soluble in ether, ethyl bromide and cold acetic acid. It crystallizes in pale yellow platelets and melts at 134°.

Other Salts.—For the purpose of comparison with the isomeric salts derived from the metoxazine a few other salts were prepared. These were obtained most easily by forming the pseudo base from the ferric chloride salt and then converting the pseudo base into the new salt.

The Chloride.—An ethereal solution containing about **1** g. of the pseudo base was saturated with dry hydrogen chloride, whereupon it gradually separated into two clear liquid layers. The top layer was decanted, the bottom layer washed, by decantation, with dry ether, then placed in a vacuum over solid potassium hydroxide. It slowly solidified, first to a glassy, finally to an opaque solid. This was dissolved in chloroform. The chloroform solution, when cooled in a freezing mixture deposited colorless needles melting at **95–97°.** The chloride is difficult to handle because it is very hygroscopic. With ferric chloride solution it forms the double chloride melting at 134°

Anal. Calcd. for $C_{15}H_{14}ONCl$: Cl, **13.6.** Found: Cl, **13.3.**

The Mercuric Chloride Salt.—This salt was made both by adding excess of saturated mercuric solution directly to the ethylation product and by adding a similar solution to the pseudo base dissolved in hydrochloric acid. It is more soluble than the ferric chloride double salt. From glacial acetic acid it crystallizes in white fluffy needles melting at **119–120°.**

Anal. Calcd. for $C_{15}H_{14}ONCl_3Hg$: Hg, **37.8.** Found: Hg, **37.8.**

With picric acid ethereal solutions of the pseudo base yielded a picrate crystallizing in yellow needles which melt at **132–133°**, and with 60% perchloric acid similar solutions formed a perchlorate melting at 183–184°.

Anal. Calcd. for $C_{21}H_{16}O_8N_4$: C. **55.8;** H, **3.6.** Found: C, **55.6;** H, **3.6.**

The Pseudo Base (III).—The pseudo base was first obtained by the usual procedure of shaking the ferric chloride double salt with sodium hydroxide in the presence of ether but it is more easily prepared directly from the ethylation mixture. For this purpose the mixture is as usual digested with hydrochloric acid and thoroughly extracted with ether. Fresh ether is then stratified on top of the sirupy liquid, the mixture is cooled with ice and sodium hydroxide solution is slowly added in excess with constant shaking. The alkaline layer is drawn off and again extracted with ether.

The ethereal extracts are combined, washed with water, dried over sodium sulfate and evaporated by suction. It leaves a pale yellow oil. This oil is dissolved in low-boiling petroleum ether and the solution is cooled to 0°. The pseudo base has a tendency to separate as oil but vigorous rubbing of the walls of the vessel with a glass rod usually induces the formation of a granular precipitate. This is recrystallized by solution in benzene and addition of petroleum ether.

Anal. Calcd. for $C_{15}H_{15}O_2N$: C, 74.6; H, 6.3. Found: C, 74.8; H, 6.3.

The pseudo base crystallizes in small prisms and melts at 79–80°. It is soluble in the usual organic solvents except petroleum ether. All operations with it must be carried out at low temperatures and as rapidly as possible because in solution it soon changes into the anhydro compound. The solid base likewise changes into the anhydro compound. At the ordinary temperature the process is relatively slow but in the course of a month all preparations turn from colorless solids to yellow oils interspersed with small droplets of water. At $-10°$, however, a sample which had been kept for a year had changed but slightly; it was pale yellow in color and its melting point had dropped two degrees.

Attempts to Prepare a Methyl Ether.—Since the ability to form methyl ethers in basic media is one of the most characteristic properties of pseudo bases of all sorts, we made many attempts to prepare such an ether. To this end we treated the ferric chloride double salt with methyl alcoholic sodium hydroxide, the chloride with sodium methylate and the pseudo base with various concentrations of alkali in methyl alcohol. All methods gave only pseudo base or, in case the experiments were too prolonged, the anhydro compound.

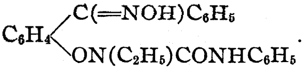
The Oxime (IV).—To a solution of 1.5 g. of the pseudo base in 10 cc. of methyl alcohol was added 1.5 g. of hydroxylamine hydrochloride and then 4 cc. of a 40% solution of potassium hydroxide. The mixture was left to itself for an hour, then poured into 80 cc. of water. The solid precipitate was washed with water, dried and recrystallized from benzene. It separated in long felted needles and melted with decomposition at 135.6°.

Anal. Calcd. for $C_{15}H_{16}O_2N_2$: C, 70.3; H, 6.3. Found: 70.4; H, 6.3.

The oxime is readily soluble in acetone, methyl alcohol and acetic acid, slightly soluble in benzene and in chloroform. To prove that it is really an oxime of the pseudo base, it was treated with dilute hydrochloric acid. It dissolved at once and when ferric chloride was added to the solution it precipitated the double salt melting at 133–134°.

The Urea Derivative (V).—To a solution of 2.4 g. of the pseudo base in 7 cc. of benzene was added 1.4 g. of phenyl isocyanate. The temperature of the solution rose rapidly to 55–60°. On cooling, the solution slowly deposited a crystalline solid. After three days the solid was recrystallized from methyl alcohol. It separated as a granular deposit which melted at 128°.

Anal. Calcd. for $C_{22}H_{20}O_3N_2$: C, 73.3; H, 5.6. Found: 73.6; H, 5.7.

The Oxime of the Urea Derivative,  $C_6H_4\left\langle\begin{array}{l}C(=NOH)C_6H_5\\ON(C_2H_5)CONHC_6H_5\end{array}\right.$.—In order to distinguish between the two possible phenyl isocyanate addition products—the urethan and the urea derivative—the substance was treated with hydroxylamine. To this end 2.2 g. of the substance and an equal weight of hydroxylamine hydrochloride were dissolved in 100 cc. of hot methyl alcohol. To this solution was added gradually 6 g. of potassium hydroxide dissolved in 8 cc. of water. The light yellow mixture was immediately cooled under the tap and set aside for twenty-four hours.

A small quantity of unchanged material was removed by filtration. The solution was diluted with 300 cc. of water and filtered again to remove a small quantity of impure product. The filtrate on acidification deposited 2.0 g. of a colorless product which was dried and recrystallized from benzene. It was thus obtained as long filmy needles resembling those of the oxime of the pseudo base. The substance melted with decomposition between 145 and 150°, depending upon the method of heating.

Anal. Calcd. for $C_{22}H_{21}O_8N_3$: C, 70.4; H, 5.6. Found: 70.5; H, 5.6.

The Anhydro Compound: **2-Methyl-4-phenyl-5,6-benzometoxazine (VII).**—As has been stated, the pseudo base spontaneously loses water and passes into the metoxazine derivative. In solution the process is rapid, hence all filtrates from the pseudo base are rich in this derivative. For preparation from the pure pseudo base the substance was heated to 95° under diminished pressure. Under these conditions bubbles of water vapor began to appear at about 60° and became brisk as the temperature rose. The residue was purified either by vacuum distillation or by transforming it into its hydrochloride, which was readily purified, and then regenerated by treatment with bases.

Anal. Calcd. for $C_{15}H_{13}ON$: C, 80.7; H, 5.9. Found: C, 80.8; H, 5 9.

When perfectly pure, the metoxazine derivative crystallizes in colorless needles melting at 33–35°. It is. however, extremely difficult to obtain it in crystalline form. It is readily soluble in all organic solvents and can be crystallized only from petroleum ether at low temperatures. It distils at 175–177° under a pressure of 11 mm. The distillate is a viscous oil which partially solidifies when its solution in petroleum ether is cooled in a freezing mixture and inoculated with solid.

The Hydrochloride.—.The hydrochloride can be made by dissolving the base in concentrated hydrochloric acid, but a better yield and a purer product are obtained by operating with dry hydrogen chloride in ether. Thus when dry hydrogen chloride was passed into a solution of 2 g. of the substance in 20 cc. of ether, a pale yellow precipitate began to form immediately. The solution was saturated, set aside for an hour, then filtered. The hydrochloride was washed thoroughly with ether, then dissolved in 4 cc. of methyl alcohol at 50° and this solution was very gradually diluted with ether to 120 cc. It deposited 2.2 g. of the hydrochloride in pale yellow needles.

Anal. Calcd. for $C_{15}H_{14}ONCl$: C, 69.3; H, 5.5; Cl, 13.6. Found: C, 69.2; H, 5.6; Cl, 13.6.

When it is heated rapidly the salt melts at 104°, but it decomposes slowly even at 110°. It is soluble in water but the solution soon becomes cloudy as it deposits the anhydro compound as a yellow oil. The metoxazine derivative itself is most easily obtained in a perfectly pure condition by adding sodium hydroxide to a solution of the hydrochloride and extracting the base with ether. The first crystals of the base were obtained by evaporating such an ethereal solution, dissolving the residual oils in petroleum ether, and keeping the mixture at −13° for several days.

The Ferric Chloride Double Salt.—Ferric chloride in excess was added to a clear solution of 3 g. of the chloride in 4 cc. of concentrated hydrochloric acid. The mixture was cooled to 6° for an hour during which it deposited the double salt in large, well-formed needles, darker in color than those of the corresponding salt of the pseudo base. The salt melted at 139–140°. When it was treated with sodium hydroxide it regenerated the metoxazine derivative.

Anal. Calcd. for $C_{15}H_{14}ONCl_4Fe$: C, 42.7; H, 3.4. Found: C, 42.7; H, 3.5.

The Picrate.—An ethereal solution of the anhydro compound was added, drop by drop, to a saturated ethereal solution of picric acid. A bright yellow solid appeared after the addition of the first few drops. After washing with ether the solid melted at 128–129°.

Anal. Calcd. for $C_{21}H_{16}O_8N_4$: C, 55.8; H, 3.6. Found: C, 55.5; H, 3.5.

The Mercuric Chloride Double Salt.—The salt was prepared like the preceding one and was purified by crystallization from acetone. It crystallized in yellow needles and melted at 180–181°.

Anal. Calcd. for $C_{15}H_{14}ONCl_3Hg$: Hg, 37.7. Found: Hg, 37.3.

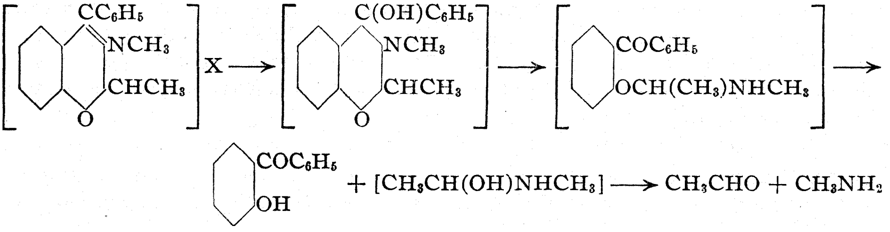
Hydrolysis of the Metoxazine Derivative.—In dilute acids the metoxazine derivative is slowly hydrolyzed. Thus when 1 g. of the substance was suspended in 25 cc of water containing one equivalent of hydrochloric acid, the color of the oil gradually became lighter and after two weeks an ethereal solution of it no longer gave a solid hydrochloride with dry hydrogen chloride. The aqueous solution, from which the oil had been removed, had a strong odor of acetaldehyde. A few drops were therefore added to a β-napthol solution and condensed according to the directions of Mulliken.[2] A precipitate formed which melted at 169°. The remainder of the aqueous solution, when evaporated to dryness, left a residue of ammonium chloride

These products—acetaldehyde and ammonium chloride—indicated that the oily hydrolysis product was probably ortho hydroxy benzophenone. The oil was therefore recovered and treated with 0.5 g. of hydroxylamine hydrochloride and 4 cc. of 40% potassium hydroxide. It turned yellow and deposited a yellow solid—a behavior which is characteristic of ortho hydroxy benzophenone.[3] The yellow color disappeared when the solution was acidified. The melting point of the crude product was 127–128". After several recrystallizations from ether it had risen to 135°, the melting point of ortho hydroxy benzophenone oxime found by Meisenheimer and Meis.[4]

Anal. Calcd. for $C_{13}H_{11}O_2N$: C, 73.2; H, 5.1. Found: C, 73.5; H, 5.2.

Cleavage with Phenylhydrazine.—Although the metoxazine derivative is very resistant to the action of aqueous alkalies it is very easily cleaved with phenylhydrazine. A mixture of 2 g. of the substance and 1.1 cc. of phenylhydrazine was heated to 130–150° for half an hour. The gas which was given off had the odor of ammonia and was identified by conversion into the picrate and into ammonium chloride. The residue in the tube was dissolved in methyl alcohol and the solid obtained in this manner was recrystallized from the same solvent. It melted at 154–155° and was identified as the phenylhydrazone of ortho hydroxy benzophenone by comparison with a sample made from the ketone obtained by acid hydrolysis. It was observed incidentally that this phenylhydrazone like a number of others is phototropic,[5] turning orange in the light and reverting to yellow in the dark.

Methylation.—Since the metoxazine derivative is an unsaturated cyclic tertiary amine, it can be methylated in the usual manner. The resulting salts are, however, extremely unstable. Even the ferric chloride double salt is rapidly hydrolyzed by water at the ordinary temperature, and the process does not stop either with the formation of the base or that of the pseudo base. It involves the metoxazine ring and proceeds until the substances are completely degraded to ortho hydroxy benzophenone, acetaldehyde and methylamine.



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[2] Mulliken, "Identification of Pure Organic Compounds," Vol. I, pp. 22–23.

[3] Cohn, Monatsh., **17,** 102 (1896).

[4] Meisenheimer and Meis, *Ber.,* **57,** 289 (1924).

[5] Chalkley, *Chem. Reviews,* 6, 233 (1929).

The Ferric Chloride Double Salt.—A mixture of 5 g. of dimethyl sulfate, which had been freed from acid by thorough washing with sodium bicarbonate and then dried over sodium sulfate, and 4.7 g. of the metoxazine derivative was heated on a steam-bath for five minutes The light brown solution was diluted with 10 cc. of concentrated hydrochloric acid and left to itself for fifteen minutes, during which time the two layers disappeared. To the clear homogeneous solution very concentrated ferric chloride was added in excess A dark brown oil precipitated. After cooling the mixture to 6° for three hours the top layer was decanted, the oil washed rapidly with cold 6 *N* hydrochloric acid, and dried over solid potassium hydroxide in a vacuum desiccator. The residue was almost completely soluble in chloroform and the solution gradually deposited 8 g. of the solid salt in deep yellow hexagonal plates. The pure salt melted at 119–120°.

Anal. Calcd. for $C_{16}H_{16}ONCl_4Fe$: C, 44.1; H, 3.7. Found: C, 44.3; H, 3.8.

Hydrolysis.—When the salt is shaken with cold dilute sodium hydroxide, or even with water, the odor of acetaldehyde appears almost immediately. For the purpose of identifying all the products of hydrolysis, one gram of the salt was shaken with 15 cc. of water until the salt was completely disintegrated. After the precipitated ferric hydroxide had been dissolved by addition of a little dilute hydrochloric acid, there remained a clear aqueous solution and a pale yellow oil.

The aqueous layer was decanted into a distilling flask and distilled to two-thirds its volume. The distillate, when treated with a solution of β-naphthol in glacial acetic acid in the usual manner, gave a precipitate of ethylidene β-dinaphthyl oxide melting at 173–174°, and therefore contained acetaldehyde. The remainder of the aqueous solution was diluted with 10 cc. of water, treated with 3 cc. of 40% potassium hydroxide and cautiously heated. The distillate was collected in 6 *N* hydrochloric acid. On evaporation it left a hydrochloride which melted at 226–227° and when this was added to a 1% solution of picric acid it formed a flaky yellow picrate which melted at 208–211°. The aqueous solution therefore contained methylamine.

The pale yellow oil was dissolved in ether. The washed and dried ethereal solution contained ortho hydroxy benzophenone, which was identified by conversion into its hydrazone and oxime.

Summary

When the salts that are obtained by alkylating 3-phenyl benzisoxazole are treated with bases they yield a pseudo base which readily loses water, and passes into an anhydro compound. The anhydro compound is a metoxazine derivative.

Since the anhydro compound can be formed only from a pseudo base which has the hydroxyl group in the 3-position, its formation shows that in the rearrangement from a base to a pseudo base the hydroxyl group may enter this position when the hindrance to every other type of rearrangement is sufficiently great.

CONVERSE MEMORIAL LABORATORY
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

4-PARA-TOLYLTHIOSEMICARBAZIDE AND ITS REACTIONS WITH KETONES

BY R. W. BOST AND W. F. SMITH

RECEIVED SEPTEMBER 25, 1930 PUBLISHED FEBRUARY 9, 1931

In spite of the fact that many substituted semicarbazides have been studied with aldehydes and ketones, it appears that the substituted thiosemicarbazides have received little attention. In view of this, we have chosen for study a substituted thiosemicarbazide which is easy to prepare, gives a good yield, and whose raw materials are fairly cheap. It was condensed with the following ketones: acetone, methyl ethyl ketone, acetylacetone, ethyl acetoacetate, cyclohexanone, acetophenone, benzophenone, benzoylacetone, benzoin, benzil and carvone.

Experimental

Di-*p*-tolylthiourea.—A method similar to that of Sell[1] was used to prepare di-*p*-tolylthiourea. An alcoholic solution of *p*-toluidine was heated under reflux for five hours with an equivalent of carbon disulfide. The pure product melted at 177°; yield, 95%.

***p*-Tolyl Mustard Oil.**—The di-*p*-tolylthiourea was converted into p-tolyl mustard oil by heating the former with acetic anhydride under reflux for fifteen minutes. The product was poured into water, steam distilled, extracted with ether and redistilled; b. p. 237°; yield, 72%.

4-*p*-Tolylthiosemicarbazide.—The method of Guba and Ray[2] was adopted. An alcoholic solution of *p*-tolyl mustard oil, cooled in an ice-bath, was treated with 42% hydrazine hydrate. The bottle containing the mixture was stoppered and shaken for a few minutes. The product was filtered and purified from alcohol. The pearly white needles melted at 137°; yield, 90%.

4-p-Tolylthiosemicarbazide Hydrochloride.—Two grams of the semicarbazide was dissolved in 20 ml. of alcohol and 5 ml. of concentrated hydrochloric acid added. On cooling, long white needles separated; m. p. 173°; yield, 90%.

Anal. Calcd. for $C_9H_{12}N_3ClS$: HCl, 16.60. Found: HCl, 16.46.

Condensation Products

To 0.01 mole of 4-p-tolylsemicarbazide dissolved in 10 ml. of alcohol was added an equivalent of the ketone. In the case of benzophenone, benzoin, benzil and carvone, 1 ml. of glacial acetic acid was added at this point. The solution was placed under reflux and heated with a hot-plate. The time of heating of the mixture depended upon the ketone. The reaction product was cooled, filtered, dried and recrystallized from alcohol. With the exception of methyl ethyl ketone and benzoylacetone, the products on cooling formed solids; even the products from these ketones, when dried and recrystallized, gave definite solids. The condensation products are also soluble in benzene and chloroform. All are soluble in ether with the exception of those from acetylacetone, benzophenone and benzoylacetone.

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[1] Sell, *Ann.*, 126, 160 (1863).

[2] Guba and Ray, THIS JOURNAL, 47, 385 (1925).

Alcoholysis of Acetylacetone-4-*p*-tolylthiosemicarbazone.—Wheeler and Norton[3] have shown that acetylacetone phenylsemicarbazide yields 3.5-dimethylpyrazole and phenylurethan when refluxed with absolute alcohol. It was found that acetylacetone-4-*p*-tolylthiosemicarbazone behaves similarly when subjected to alcoholysis.

Three-tenths gram of acetylacetone-4-p-tolylthiosemicarbazone was dissolved in 10 ml. of absolute alcohol and refluxed for one hour. The alcohol was evaporated on a steam-bath, leaving a colorless oil which crystallized on cooling. The residue was extracted with 5 ml. of water. A small quantity of yellow oil was insoluble. The water solution was evaporated to 1 ml. on a steam-bath. On standing overnight, small colorless flakes of 3.5-dimethylpyrazole appeared. They melted at 105–106°. The oil insoluble in water was crystallized from petroleum ether, whereupon a small quantity of a crystalline substance melting at 69–74" was obtained. It possessed an odor similar to that of anisole. The substance was undoubtedly *p*-tolylthiourethan. No analysis could be made because of a lack of sufficient material.

TABLE I

DATA ON DERIVATIVES

No.	Ketone	Form	Solvent	M. p., °C.	Time heated, minutes	Formula	Sulfur analyses, % Calcd.	Sulfur analyses, % Found
1	Acetone	Colorless plates	Alcohol	142[4]	1	$C_{11}H_{15}N_3S$	14.48	14.65[4]
2	Methyl ethyl	Colorless plates	Alcohol	75	10	$C_{12}H_{17}N_3S$	13.52	13.68
3	Acetylacetone	Fine white needles	Alcohol	100	5	$C_{13}H_{17}ON_3S$	12.09	11.99
4	Ethyl aceto-acetate	Fine white needles	Alcohol	107	15	$C_{14}H_{18}N_3S$	10.86	10.79
5	Cyclohexanone	Long white needles	Alcohol	125	15	$C_{14}H_{19}N_3S$	12.18	12.24
6	Acetophenone	Bulky white needles	Alcohol	165	15	$C_{16}H_{17}N_3S$	11.24	11.17
7	Benzophenone	Pale yellow needles	Alcohol	158	120	$C_{20}H_{19}N_3S$	9.23	9.32
8	Benzoylacetone	Pale yellow plates	Alcohol	126	15	$C_{18}H_{19}N_3S$	9.80	9.85
9	Benzoin	Cream-colored needles	Alcohol	161	60	$C_{22}H_{21}ON_3S$	8.50	8.39
10	Benzil	Fine cream-colored needles	Alcohol	164	120	$C_{22}H_{19}ON_3S$	8.55	8.52
11	Carvone	Fine cream-colored needles	Alcohol	147	45	$C_{23}H_{25}N_3S$	10.17	10.25

Conclusions

1. 4-*p*-Tolylthiosemicarbazide has been prepared in good yields.
2. It was condensed with the following ketones: acetone, methyl ethyl ketone, acetylacetone, ethyl acetoacetate, cyclohexanone, acetophenone, benzophenone, benzoylacetone, benzoin, benzil and carvone.

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[3] Wheeler and Norton, THIS JOURNAL, 50, 2488 (1928).

[4] Froom, Kapeller and Krauss, *Ann.*, 447, 234 (1926).

3. 4-*p*-Tolylthiosemicarbazide reacts readily with the above ketones to give easily purified solid derivatives having definite melting points.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE]

THE INFLUENCE OF THE HALOGENS ON THE COLOR OF AZO DYES. THE SPECTRAL ABSORPTION OF CERTAIN MONO-AZO DYESTUFFS

BY DUNCAN GRAHAM FOSTER

RECEIVED OCTOBER 28, 1930 PUBLISHED FEBRUARY 9, 1931

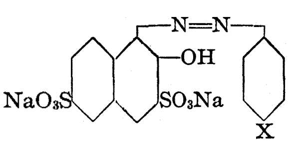
Introductory

Some years ago the author participated in one of a series of investigations on the relation of molecular structure to the color of azo dyes.[1] The influence of o-, *m*- and p-substitution of sulfur and oxygen was studied,[2,3,4] and the preparation of dyes containing selenium is now under way.[5]

In all of this work color comparisons were made simply by the inspection of dyed samples. Recently the method of color analysis made possible by the development of the spectrophotometer has reached a stage where it is particularly valuable for this kind of study, and we hope that eventually all of the many dyes prepared in the investigations mentioned above may be quantitatively compared by means of this instrument.

This paper reports measurements of the spectra of dyes containing another group of the periodic system, the halogen family, with the spectrophotometer, to show the effect of o-, m- and p-substitution of chlorine, bromine and iodine. We attempted also to measure their absorption in the near ultraviolet with a quartz spectrograph and a densitometer, but because of the crudity of the apparatus were not able to obtain accurate results, and so have postponed this work until better instruments shall be available.

Preparation of the Dyes.—In order to preserve continuity with the dyes already studied, we selected dyes prepared by coupling an amine containing the halogen atom with R-salt. These compounds had the structure I, in which X is the halogen atom, shown here in the *p*-position. The o-, *m*- and *p*-chloro-, bromo- and iodo-anilines used were either bought on the market (Eastman Kodak Co.) or made by reduction of the corresponding halogeno nitrobenzene. In the latter case the amine was isolated as the hydrochloride.[1]



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[1] Foster and Reid, THIS JOURNAL, 46, 1936 (1924).

[2] Waldron and Reid, *ibid.*, 45, 2399 (1923).

[3] Holt and Reid, *ibid.*, 46, 2329; 46, 2333 (1924).

[4] Palmer and Reid, *ibid.*, 48, 528 (1926).

[5] See Foster and Brown, ibid., 50, 1182 (1928).

The purity of these compounds was established by the sharpness of the melting or boiling points. Solid compounds were recrystallized and liquid ones redistilled, if necessary, to melt or boil over a range of not more than one degree, and in most cases the melting or boiling range was less than this. Further purification was effected in the double (in some cases triple) recrystallization of the dyes themselves. There is, of course, no way of estimating the presence of a para compound in its ortho analog or *vice* versa, but this purification was felt to be amply sufficient to prevent the spectrum from being affected. Meta dyes, because of the different method of preparing the intermediate, could not be contaminated with the other isomers.

The amines were diazotized and coupled with R-salt by the standard method previously employed.[2] The dye made by coupling aniline with R-salt, which is the parent substance of the whole group, was prepared for use as a control. These compounds were all twice (at least) recrystallized from hot water. Because they were sodium salts and had no melting points, there was no criterion of purity, but sodium chloride, from the salting-out of the dye, is the only impurity likely to be present and this would not interfere with the spectral absorption. For purposes of making up standard solutions, the analyses gave us the amount of pure dyestuff present, and in point of fact it later developed that water was the chief contaminant of the solid dyes.

Analysis of the Dyes.—The dyes were analyzed both as dried samples and as indeterminate solutions made from the same samples. These indeterminate solutions were then used as stock solutions to make up the final solutions examined by the spectrophotometer. The method used was that of titration with titanous chloride, which is both rapid and accurate.[6]

Quantities sufficient to make 1 liter of $M/50$ solution were weighed roughly, dissolved in hot water and made up to 1 liter in a volumetric flask; 25-ml. titers were measured with a Bureau of Standards pipet and an excess of standard titanous chloride solution added from a buret. The excess was then determined with standard ferric ammonium sulfate solution, using ammonium thiocyanate as an indicator. This gave the amount of dyestuff in the solution and enabled us to calculate the volume that must be taken to make an exactly 5×10^{-5} molar solution, when diluted to one liter.

All the data thus obtained are given in Table I, in which the figures are the average of three determinations in each case.

The low percentages of dyestuff in each dry sample were due to the fact that the dyes are highly hygroscopic and took up moisture perceptibly

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[6] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co.

TABLE I

ANALYTICAL DATA

Dye	Wt. of dye for 1 liter of 5×10^{-5} *M* soln.	Dry dye found, %	Stock solution for 1 liter of 5×10^{-5} soln., ml.
Aniline	0.0229	87.20	23.20
o-Chloro	.0243	87.37	25.51
m-Chloro		90.80	23.15
p-Chloro		80.20	26.88
o-Bromo	.0266	92.40	20.78
m-Bromo		85.24	24.30
p-Bromo		90.28	26.92
o-Iodo	.0289	90.80	21.87
m-Iodo		97.10	22.52
p-Iodo		86.57	30.36

while being weighed. The m-iodo dye, for example, after drying for one hour at 85° and cooling in a desiccator, gained 4 mg. while weighing. The same sample, dried for one hour at 100°, cooled in a desiccator and rapidly weighed gave 97.10% of dye, the highest percentage obtained. All the others were exposed to the air for twenty-four hours to insure that their aqueous tension had reached that of the atmosphere. These samples were not used in making up our solutions for examination, so that the high moisture content has no effect on the final concentration.

Preparation of the Solutions.—Preliminary trials showed that a concentration of 5×10^{-5} molar was the most satisfactory to use in the spectroscopic examination. These solutions were made by measuring from a Bureau of Standards buret exactly (to 0.02 ml.) the quantity of the stock solutions described above required by the analysis to give this concentration when diluted to one liter. These quantities were diluted, with careful adjustment for temperature, in a Bureau of Standards volumetric flask, first adding from a pipet 10 ml. of a buffer solution of sodium acetate and acetic acid. This buffer was kept in stock in such concentration that 10 ml. would give a solution 0.01 N in both sodium acetate and acetic acid in the final volume of 1 liter. These solutions were freshly prepared within three to four hours before using.

That this method of analysis and preparation of solutions was of satisfactory accuracy was checked by repeating the spectral measurements in two cases with solutions made up freshly from dry dyestuff, analyzed separately and diluted to give the necessary concentration. These "repeat experiments" gave spectral absorption curves coincident with the originals, within the limitations of the instrument (see below).

Determination of the Spectral Absorption.—For the color analysis a Keuffel and Esser Color Analyzer was used,[7] modified for use only with

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[7] This instrument and its accessories were put at the author's disposal through the kindness of the Technical Laboratory of the E. I. du Pont de Nemours Company, which the author hereby gratefully acknowledges.

solutions and reading directly the negative logarithm of the transmittancy. The cells were a special open-topped type made wholly of optical glass and were especially easily cleaned and filled. They offered a solution thickness of 10 mm. They were filled with a broad-tipped pipet and both pipet and cell were washed three times with solution before filling. Readings were taken at intervals of 10 millimicrons, first setting the wave length scale at the desired figure. Three readings agreeing within the limit of accuracy were made for each setting. This limit varies with the wave length and runs from about 0.002 of a unit at 700 millimicrons to about 0.1 of a unit at 450 millimicrons, the range over which determinations were made. Whenever it seemed necessary, particularly at the peaks and shoulders of the absorption bands, readings were taken at intervals of 5 millimicrons.

To check the accuracy and guard against personal error, a standard glass No. G. **586-A** was measured and checked after measurement against figures published by the Bureau of Standards. The measurements were found to agree with the Bureau of Standards figures within the above limits. The instrument itself was also checked for adjustment at maximum and minimum transmittancy before each half-day's work.

Calculation of Results and Plotting of Graphs.—The values determined and plotted are the negative logarithms of the transmittancy of the dye solution at given wave lengths. The *transmittancy* is defined as the ratio of the *transmittance* of the solution to that of the solvent, or $T_{\text{sol.}}/T_{\text{sov.}} = \mathbf{T}$.[8] The negative logarithm of this value represents as nearly as possible the way the color appears to the eye. In this paper these values are plotted from the top downward as abscissas, against the wave length as ordinates.

Discussion of Results

Examples of the spectral absorption curves obtained are given in the figures. Because no striking differences were observed, we are publishing one set of curves only and one "analyzed" curve, in order to economize space. In Fig. 1 the isomeric *o*-, *m*- and *p*-chloro derivatives are plotted together to show the difference between them. The color of all the dyes was red, with the chief absorption band in the violet portion of the spectrum, at almost the same wave length in every case. When dyed to 2% dyeings on wool flock they showed differences in shade easily visible to the naked eye, in the same directions but of a lesser magnitude than had been shown by the corresponding dyes containing sulfur.

It was obvious from the graphs that the color difference is a complex phenomenon, not due to a simple change in the magnitude or position of the chief absorption band. Thus a color that appears deeper red to the

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[8] *For detailed definitions see Brode, Bureau of Standards Journal of Research,* 2, *502* (1929).

eye than another may have a lesser absorption in the red portion of the spectrum or a deeper absorption in the violet, or both. It may also have quite different characteristics in the yellow or green or even a uniform difference throughout the entire range preceding the chief absorption band. This last effect is shown most strikingly by the three bromo dyes, which exhibit absorption curves parallel but of slightly different depth throughout the whole of this range.

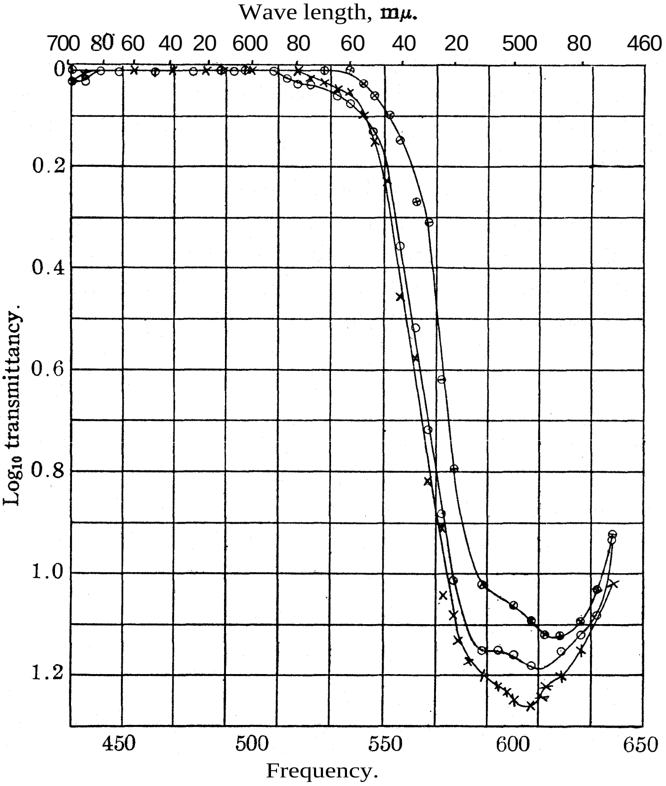

Fig. 1.—Chlorine dyes: O, ortho; ⊕, meta; ×, Para.

There is no uniformity even in the influences of position isomerism, for the depth of the absorption band for the chloro and bromo dyes increases in the order meta, ortho, para; while with the iodo dyes this sequence is ortho, meta, para. From the data obtained it is extremely difficult to make any generalizations.

The irregularities appearing near the peaks of the absorption bands appear as well in all the other dyes not shown in the figures. The iodine dyes, in fact, show two of them, one on either side of the peak of the band. We do not believe that these are accidental, since repetitions of the measurements in two instances, made two days apart with fresh solutions, gave the same results.

Rrode has observed the same effect with other dyes and has suggested that it is due to the presence of two or more component bands partly superimposed upon each other.[9] According to him these component bands are

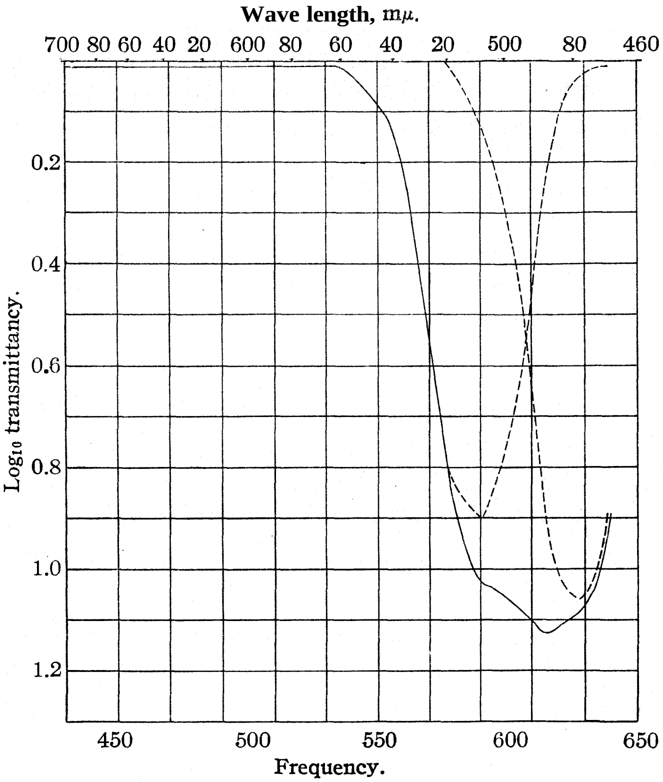

Fig. 2.—Analysis of the spectral curve of the *m*-chloro dye into its components. The solid curve is the experimental curve, the dotted curves the components, so drawn that the sum of the abscissas of the component curves at any point equals the abscissa of the experimental curve at the same point.

caused by two or more color-absorbing constituents of the dye molecule in equilibrium with each other, and the absorption curves can be analyzed to show their position and shape. Such an analysis for the *m*-chloro dye is shown in Fig. 2.

In general, the shift in the magnitude of the chief absorption bands due to position isomerism is in accord with the observations to be found in the literature. *p*-Substitution brings about a marked increase in depth, *o*-

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[9] Reference 8 above, p. 520.

substitution a decrease and m-substitution a less marked decrease. The only exception to these rules are our m-chloro and m-bromo dyes, which show a greater decrease than the corresponding o-compounds.

Summary

1. A series of dyes containing the three halogens in the o-, *m*- and **p**-positions have been prepared, their spectral absorptions in water solution determined and compared with that of a parent dye containing no halogen.

2. The results show no simple relationship between the dyes attributable to variations in molecular weight but a complicated effect distributed in different portions of the spectrum.

3. The effect of position isomerism is for the most part the same as that observed by other workers.

4. The chief absorption bands appear to be composed of two or more constituent bands. These have in one instance been calculated.

SWARTHMORE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY NO. 650]

RESEARCHES ON THIAZOLES. XVI. THE SYNTHESIS AND STUDY OF NEW AMINOTOLUTHIAZOLES AND DERIVATIVES FROM 2,5-DIAMINOTOLUENE-4-THIOSULFURIC ACID

BY MARSTON TAYLOR BOGERT AND MANASSEH G. SEVAG

RECEIVED NOVEMBER 6, 1930 PUBLISHED FEBRUARY 9, 1931

Following up the work already reported[1] from these laboratories on benzothiazole dyes, incidental and related compounds, it seemed to us desirable to ascertain the tinctorial properties of such dyes when they carried also free amino groups in the molecule, and the present paper is a contribution to the solution of the problem, in that it describes a method by which the necessary intermediates may be synthesized and records some preliminary experiments in the preparation therefrom of dyes of the Columbia Yellow (Colour Index No. 814) class.

The initial material was the 2,5-diaminotoluene, which was converted into a monothiosulfuricacid by the method of Bernthsen.[2] Theoretically, such a derivative might possess any one of the structures I, II or III, all of which are capable of yielding benzothiazoles. Thus, if condensed with *o*-nitrobenzaldehyde, they should give the thiazoles IV, V and VI, respectively, elimination of whose amino groups should result in the production of VII, VIII and IX.

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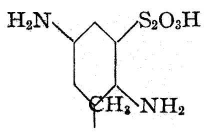
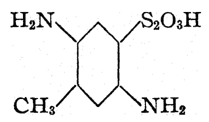
[1] (a) Bogert and Bergeim, *Color Trade J.*, 15, 63 (1924); (b) Bogert and Allen, *Ind. Eng. Chem.*, 18, 532 (1926); (c) Bogert and Allen, THIS JOURNAL, 49, 1315 (1927).

[2] Bernthsen, *Ann.*, 251, 61 (1889).



I



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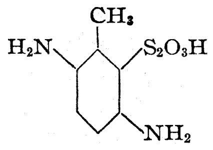
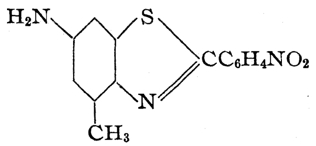
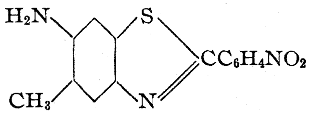


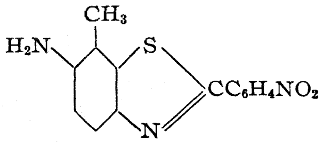
III



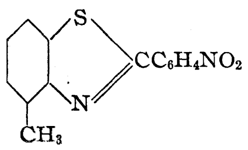
IV



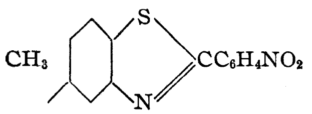
V



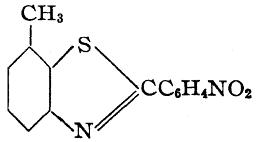
VI



VII



VIII
(M. p. 91–92°)



IX
(M. p. 108.5°)

Of the last three compounds, VII has not yet appeared in the literature, but VIII and IX have been described by Bogert and Allen.[3]

When this series of reactions was carried out with our 2,5-diaminotoluene thiosulfuric acid, the nitrotoluthiazole obtained as the final product proved to be identical with VIII. Hence the —SSO_3H group in the initial acid must have been in Position 4, *i. e.*, the acid must have had structure II.

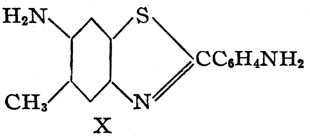
Potentiometric titrations were carried out with the acid and the results plotted graphically. From these results, the ionization constant of the acid was calculated as 5.56×10^{-6} at 25°.

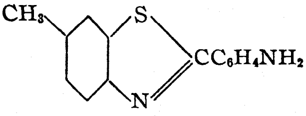
Condensation of the thiosulfuric acid with *o*-, m- and *p*-nitrobenzaldehydes, or with 2,4-dinitrobenzaldehyde, led to the formation of the expected toluthiazoles, except in the case of the *p*-nitro compound where two moles of the aldehyde participated in the reaction, resulting in the production of a p-nitrobenzalamino, instead of a simple amino group, in Position 6 of the benzothiazole nucleus.

This p-nitrobenzalamino group was remarkably resistant to hydrolyzing agents, and this stability was associated in some manner with the presence of the nitro groups, for when the compound was treated with tin and hydrochloric acid, the nitro group on the 2-phenyl nucleus was reduced and the p-nitrobenzalamino at 6 simultaneously hydrolyzed to the 6-amino, giving the 2-(*p*-aminophenyl)-5-methyl-6-aminobenzothiazole.

[3] Bogert and Allen, THIS JOURNAL, 49, 1320 (1927).

The other 2-aminophenyltoluthiazoles were secured by reduction of the corresponding 2-nitrophenyl derivatives, save the m-amino compound, which could not be isolated in sufficient purity for analysis. These products are analogous to the well-known dehydrothio-*p*-toluidine, and the intention is to use them in similar ways as dye intermediates:


X


XI

The 2-(*p*-aminophenyl) derivative (X), for example, differs from dehydrothio-*p*-toluidine (XI) only in the location of its methyl group, a difference which we have shown in a previous communication'' to be without any great effect upon the shade, and in the presence of an additional amino group upon the benzothiazole portion of the molecule.

Preliminary experiments have shown that the 2-(*o*- and *p*-aminophenyl) derivatives can be converted into direct cotton dyes of the Columbia Yellow class, in which the amino group in Position 6 remains intact: and that these amino Columbia Yellow dyes, when diazotized and coupled, yield azo dyes which are also substantive for cotton.

Experimental Part

2,5-Diaminotoluene-4-thiosulfuric Acid, $CH_3(1)(NH_2)_2(2,5)C_6H_2SSO_3H\text{-}(4)$.—The 2,5-diaminotoluene which served as initial material for this research was generously supplied by the Fales Chemical Co. of Cornwall, N. Y., and was an exceptionally high-grade product which, when freshly distilled, formed colorless needles, m. p. 64°, b. p. 273" It was preserved in the form of its hydrochloride and used as such in the experiments.

For its conversion into the thiosulfuric acid, the method used by Bernthsen[2] for the preparation of *p*-phenylenediamine thiosulfuric acid was utilized, with one or two modifications. The best results were obtained when the materials were used in the proportion of seven moles of the diamine hydrochloride, seven moles of sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$), one mole of potassium dichromate, and 50 g. of aluminum sulfate.

To a solution of 50 g. of diaminotoluene hydrochloride in 120 cc. of water. there was added 50 g. of powdered aluminum sulfate, and then a solution of 64 g. of sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$) in 120 cc. of water was stirred in slowly. A copious white precipitate separated, which was probably the thiosulfate of the diamine.[4] To this mixture, a solution of 10 g. of potassium dichromate in 120 cc. of water was added gradually (during about one minute). The precipitate largely redissolved and the solution turned green at first, changing finally to a dark purplish-green.

After standing for a few minutes, it was filtered and the filtrate, after six to ten hours, separated a small quantity of a dark red amorphous solid, which was likewise filtered out. From the filtrate so obtained, the diamine thiosulfuric acid crystallized after forty-eight to seventy-two hours' standing, in dark steel-gray rhombic crystals; yield, 15%.

This product was purified by suspending the finely powdered material first in alcohol and then in ether for several hours, repeating the treatment until the decanted washings were nearly colorless. This removed the organic impurities. The product

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[4] Wahl. *Compt.* rend., 133, 1216 (1902).

so purified was washed several times with tepid water and a solution of citric acid, to eliminate any traces of iron which might have been present in the initial diamine, since iron if present is likely to be carried down and retained by the diamine thiosulfuric acid.

The purified compound, when heated in an open crucible, decomposed without melting, swelling up and taking fire.

Anal. Calcd. for $C_7H_{10}O_3N_2S_2$: C, 35.88; H, 4.27; S, 27.40. Found: C, 35.88; H, 4.42; S, 27.64.

In carrying out the above method of preparation, it was found necessary to work with small batches only, since when quantities were used much larger than those stated, the yields were lower and the products less pure.

The location of the thiosulfuric acid group in this compound was proved, as described heyond, by condensing it with o-nitrobenzaldehyde to the 2-(*o*-nitrophenyl)-aminotoluthiazole, removal of whose amino group yielded the 2-(*o*-nitrophenyl)-5-methylbenzothiazole, from which it follows that the —SSO_3H group must have been in Position 4.

Potentiometric Titration of 2,5-Diaminotoluene-4-thiosulfuric Acid.—In a 100-cc. volumetric flask containing 100 cc. of distilled water there was suspended 0.1 g. of the thiosulfuric acid and this was brought into solution by shaking. This solution was transferred to a pyrex hydrogen gas electrode vessel, the flask being rinsed out with 25 cc. of water and this rinsing added to the main solution. The cell was connected to the saturated calomel electrode by a glass-stoppered salt bridge filled with saturated potassium chloride solution. The titration was conducted at 25° in a gas-tight apparatus, using a Type K potentiometer, in an atmosphere of hydrogen which had been purified by passing over heated copper oxide. The calomel and hydrogen electrodes were standardized by determining potentiometrically the P_H of a 0.104 *N* hydrochloric acid solution. Calculated P_H for 0.104 *N* HCl, 1.01; found, 0.99.

The titrations were carried out by means of a 0.0202 *N* sodium hydroxide solution, the stoichionietrical point for which was 21.3 cc. For reasons explained in what follows, a reverse titration also was conducted using 0.0202 N hydrochloric acid. The results of these titrations are presented graphically in the curves shown.

In the course of titration it was noticed that, after reaching a certain stage in the experiment, the potential began to drop to a final equilibrium much lower than the initial one. This phenomenon occurred only within the range of P_H 7.66 (0.6988 volt) to P_H 9.58 (0.8124 volt). These figures represent the initial readings. Final equilibrium corresponding to P_H 7.66, after seventy-five minutes, was 7.51 (or 0.6908 volt), and that corresponding to P_H 9.58 after twelve hours was 9.36 (or 0.7993 volt). The drop of potential took place at every point within this range after the addition of sodium hydroxide, and was a minimum at either of these two points, and maximum at P_H 8.71 (or 0.7612 volt). The final equilibrium corresponding to P_H 8.71 was P_H 7.97 (or 0.7177 volt), after thirty hours, a drop of 0.74 P_H unit (or 0.0435 volt).

The final neutralization equilibrium was easily attained at all points corresponding to measurements up to *P*H 7.66 (or 0.6988 volt), and above PH 9.58 (or 0.8124 volt).

The phenomenon within the above mentioned range may be due to one of the following causes: (1) decomposition of the diamine thiosulfuric acid with formation of sulfuric acid; (2) poisoning of the electrode by some impurity present in either the thiosulfuric acid or the sodium hydroxide (3) liberation of hydrochloric acid occluded by the electrode during the process of platinizing in chloroplatinic acid, or occlusion of the diamine thiosulfuric acid in which the electrode was immersed.

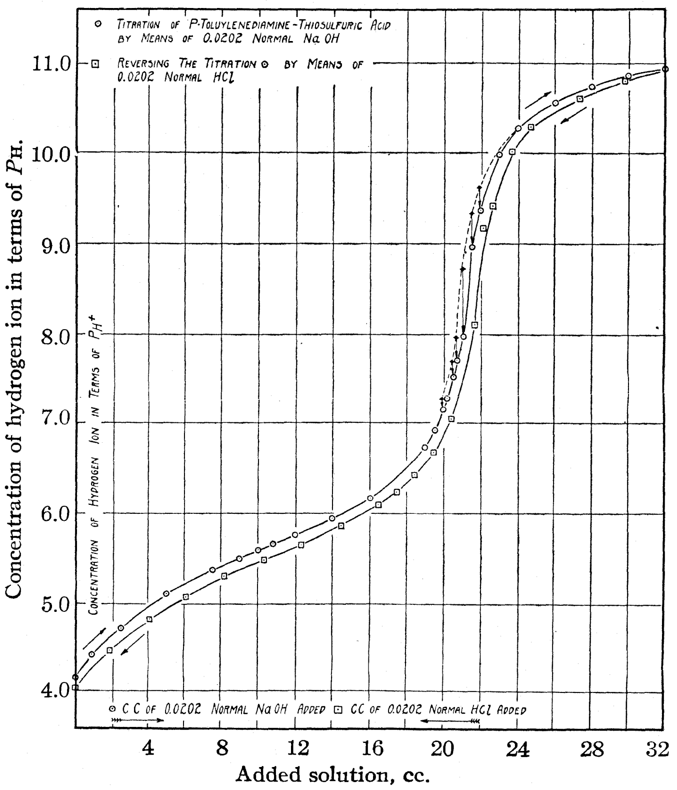

Fig. 1.

It was shown that there was no decomposition of the diamine thiosulfuric acid with formation of sulfuric acid because the final equilibrium remained constant for sixty-three hours and because practically no barium sulfate could be obtained from the solution after standing for twenty-four hours. Poisoning of the electrode was proved not to occur as shown by the smoothness of the curve, the similarity of the reverse titration curve and the constancy of the electrode after eighty hours' standing in solution.

'The third hypothesis concerning the drop in potential suggested the liberation of the hydrochloric acid occluded by the electrode during the process of platinizing in chloroplatinic acid solution, and the diamine thiosulfuric acid occluded by the electrode during the period before reaching the neutralization region. In order to determine whether the electrode contributed to the occurrence of this phenomenon, a new electrode was platinized under similar conditions and used to titrate 25 cc. of 0.1 *N* hydrochloric acid solution diluted to 125 cc. with distilled water. The steady neutralization equilibrium was obtained immediately at each point and no indication of drop of potential was observed during the entire course of titration. The curve plotted from the results was a typical hydrochloric acid titration curve. However, due to the fact that in the measurements of hydrogen electrode potentials in inorganic solutions which are strongly acid, strongly alkaline, or well buffered, it is difficult to observe this phenomenon,[5] it was necessary to study the measurements of the hydrogen electrode potentials of an organic acid whose ionization constant approximated that of the diamine thiosulfuric acid.

According to Ostwald,[6] *Ka* for propionic acid from the conductivity measurements is 1.34 X 10^{-6}. One hundred cubic centimeters of 0.0052 normal propionic acid was titrated by means of 0.0197 normal sodium hydroxide solution. In the course of the titration it was noticed also in this case that after reaching a certain point in the titration, the potential began to drop to a final equilibrium which was much lower than the initial potential. This drift of potential occurred within the range of PH 7.85 (0.7104 volt) to 8.91 (0.7730 volt) The final reading of potential corresponded to 0.7104 at 0.6504, a drop of 0.0170 volt. Beyond this point if any drift of potential was noticed it was upward in trend. A comparison of these results with those obtained from the measurements of the hydrogen electrode potentials of the diamine thiosulfuric acid will at once show a close resemblance and point to a common cause. Beans and Hammett,[5] from their studies on the hydrogen electrode, conclude that the greatest single cause of this phenomenon is the overwhelming tendency of platinum to occlude substances of an acid nature and to give up the occluded acid slowly but continuously. Therefore, in the light of these observations, the phenomenon observed in this investigation may be attributed to the occlusion of acids.[7] The molecular weight calculated from the stoichiometrical point of the final equilibrium curve is the one that approximates

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[5] Beans and Hammett, THIS JOURNAL, 47, 1215 (1925).

[6] Ostwald, Z. *physik. Chem.*, **3**, 170, 241, 369 (1889).

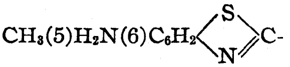
[7] From the conductivity measurements at 25°, the ionization constant for propionic acid, according to White and Jones [THIS JOURNAL, 44, 197 (1910)], is 1.4 X 10^{-5}; Franke [*Z. physik. Chem.*, **16**, 463 (1895)], 1.3 X 10^{-5}; Drucker [ibid., 52, 641 (1905)], 1.3 × 10^{-5}. The shape of the titration curve plotted from our measurements is similar to that of acetic acid with an ionization constant of 1.86 X 10^{-5}.

most satisfactorily to the true molecular weight. This relationship is suggestive of the possibility of the diamine thiosulfuric acid having been occluded by the electrode to a greater extent than the hydrochloric acid from the chloroplatinic acid solution during the process of platinizing the electrode.

Ionization Constant of **2,5-Diaminotoluene-4-thiosulfuric** Acid.—It has been found that the hydrogen-ion concentration in a weak acid 50% neutralized by a strong base is equal to that of the acid provided the salt is practically completely ionized; that is, the middle point of the titration curve of a given acid lies near the point where the hydrogen-ion concentration is numerically equal to the dissociation constant.

In the titration of the diamine thiosulfuric acid, the middle portion of the titration curve corresponds to 10.65 cc. of the sodium hydroxide, or P_H 5.64, or $C_H = 5.56 \times 10^{-6}$. Hence $Ka = 5.56 \times 10^{-6}$.

2-(*o*-Nitrophenyl)-5-methyl-6-aminobenzothiazole,



$CH_3(5)H_2N(6)C_6H_2<^{S}_{N}>C-C_6H_4NO_2(o\text{-})$.—A mixture of 10 g. of the diaminotoluene thiosulfuric acid, 8 g. of o-nitrobenzaldehyde and 80 cc. of glacial acetic acid was refluxed gently for twenty to thirty minutes and then more strongly for an hour longer. The color of the mixture gradually turned to *a* dark red, and considerable bumping occurred due to the separation of a cream-colored precipitate, which was possibly the acetate of the desired product. The mixture was filtered hot and more of the precipitate separated from the filtrate as the latter cooled and was added to the original precipitate. Warmed on the water-bath with caustic alkali, this cream-colored substance was changed to a yellow solid. Seven grams of the former gave 5 g. of the latter, which proved to be the compound sought

The filtrate from the cream-colored precipitates was diluted carefully to incipient turbidity and concentrated at laboratory temperature by allowing a stream of dry air to impinge upon its surface. The thiazole separated gradually and nearly completely. Crystallized from 90% alcohol, it was obtained in yellowish needles, m. p. 144° (corr.); yield 36%.

Anal. Calcd. for $C_{14}H_{11}O_2N_3S$: C, 58.94; H, 3.86; S, 11.24. Found: C, 58.86; H, 3.99; S, 11.38.

The alcoholic solution of these crystals exhibited a very faint purplish-red fluorescence.

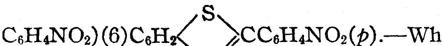
A small amount (*0.5* g.) of this thiazole was diazotized at 0° and after the diazotized mixture had stood for thirty minutes at that temperature it was filtered and the precipitate suspended in 30 cc. of concentrated formic acid and exposed for three hours to direct sunlight. This suspension was refluxed for ten minutes and the resulting solution poured into cold water. The pale yellow precipitate which separated was removed and crystallized from 60% alcohol in lustrous pale yellow needles, m. p. 91.5–92°, which is the melting point recorded by Bogert and Allen[3] for 2-(*o*-nitrophenyl)-5-methylbenzothiazole.

Anal. Calcd. for $C_{14}H_{10}O_2N_2S$: N, 10.37. Found: N, 10.59.

2-(m-Nitrophenyl)-5-methyl-6-aminobenzotoe was synthesized from the diamine thiosulfuric acid and m-nitrobenzaldehyde in much the same way as just described for the o-nitro isomer.

During the refluxing of the initial mixture, some bumping also occurred, caused by the separation of by-products. Upon the completion of the heating, the mixture was filtered hot and as the filtrate cooled most of the thiawle separated, due to its sparing solubility in cold glacial acetic acid. The filtrate from this thiazole was diluted to moderate turbidity and then heated. This caused the impurities to redissolve and by filtering the hot solution more thiazole was recovered. Too large dilution during this latter step obviously precipitated more tarry impurities than could be redissolved on heating. The crude thiazole was refluxed in a large volume of glacial acetic acid in the presence of a decolorizing charcoal, to remove tarry impurities, and then crystallized from toluene, from which it separated very slowly in orange-yellow needles, m. p. **233** 5° (corr.); yield, 58.5%. In toluene solution it showed a yellowish-red fluorescence.

Anal. Calcd. for $C_{14}H_{11}O_2N_3S$: C, 58.94; H, 3.86. Found: C, 58.76; H, 3.99

2-(*p*-Nitrophenyl)-5-methyl-6-(*p*-nitrobenzalamino)-benotazole $CH_3(5)(N=C_6H_4NO_2)(6)C_6H_2$  $C_6H_4NO_2)(6)C_6H_2\langle{}^{S}_{N}\rangle CC_6H_4NO_2(p)$.—When a mixture of 11 g. of the diamine thiosulfuric acid, 15 g. of *p*-nitrobenzaldehyde and 75 cc. of glacial acetic acid was refluxed, the reaction seemed to proceed in the same way as noted for the *o*- and m-isomers A dark red solid precipitated which, when removed and crystallized from xylene, yielded fine dark red needles, m. p. 279" (corr.), the xylene solution exhibiting a greenish-yellow fluorescence. More of this materiai was precipitated from the original acetic acid mother liquor by diluting the latter with alcohol and warming.

Anal. Calcd. for $C_{21}H_{14}O_4N_4S$: C, 60.30; H, 3.32; N, 13.4; S, 7.65. Found: C, 60.00, 60.15, 60.22; H, 3.91, 3.94, 3.68; N, 13.24; S, 7 67.

While these analytical results are reasonably satisfactory so far as C, N and S are concerned, it is not clear why the figures for hydrogen should run so high.

A determination of the molecular weight gave the figures 405.1 and **411.4;** calcd., 418.

A careful search for 2-(*p*-nitrophenyl)-5-methyl-6-aminobenzothiazole in the mother liquors from the *p*-nitrobenzal derivative resulted in the isolation, finally, through repeated fractional crystallization, of a very small amount (0.005 *g.)* of fine bright orange needles, m. p. 312–315°, whose analysis indicated that they were probably the impure amine. but the quantity remaining after the analysis was insufficient for further purification.

Anal. Calcd. for $C_{14}H_{11}O_2N_3S$: C, **58.94;** H, 3.86. Found: C, 57.72; H, 3.00.

Attempts to prepare this amine by varying the proportions of initial materials, temperature, length of heating, and other factors, gave only the *p*-nitrobenzal derivative.

This *p*-nitrobenzal derivative was surprisingly stable to hydrolysis, for it was unaltered when refluxed for several hours with either 30% sulfuric or concentrated hydro chloric acid. This stability was evidently associated with the presence of the nitro group for, as described beyond, when subjected to the action of tin and hydrochloric acid, the reduction of the nitro groups was accompanied also by hydrolysis of the *p*-nitrobenzalamino group.

A small amount (1.0 g.) of the 2-(*p*-nitrophenyl)-5-methyl-6-(*p*-nitrobenzalamino)-benzothiazole was treated with 25 cc. of cold concentrated nitric acid for one or two minutes and the mixture then diluted with water. The precipitate separated crystallized from xylene in fine reddish orange needles, which melted at 247.5° (corr.), then congealed and remained unmelted at 300°. The product was apparently an impure mononitro derivative of the *p*-nitrobenzalamino compound

Anal. Calcd. for $C_{21}H_{13}O_6N_5S$: C, 54.42; H, 2.67. Found: C, 54.24; H, 3.41.

2-(*o,p*-Dinitrophenyl)-5-methyl-6-aminobenzothiazole was prepared by refluxing for an hour and a half a mixture of the diamine thiosulfuric acid (10g.), 2,4-dinitrobenzaldehyde (15 g.) and glacial acetic acid (80 cc.) and filtering hot. The small quantity of insoluble material filtered out was composed largely of the acetate of the thiazole, from which the thiazole itself was recovered by treatment with alkali.

The main portion of the thiazole was obtained from the filtrate by concentrating it cold with the aid of a current of air, adding alcohol to the concentrate, collecting the precipitate and crystallizing it from benzene. Fine red needles resulted, m. p. 239.2' (corr.); yield, 30%. A benzene solution of the compound possessed a greenish fluorescence.

Anal. Calcd. for $C_{14}H_{10}O_4N_4S$: C, 50.90; H, 3.03 Found: C, 51.03; H, 3 12.

2-(*o*-Aminophenyl)-5-methyl-6-aminobenzothiazole.—The 2-(*o*-nitrophenyl)-5-methyl-6-aminobenzothiazole (4 g.) was dissolved in concentrated hydrochloric acid (25 cc.) and refluxed for two hours with tin (10 g.), after which the excess of tin was filtered out, the filtrate diluted with an equal volume of water, then made strongly alkaline with sodium hydroxide solution and allowed to cool. The precipitate was removed and rubbed to a paste with strong sodium hydroxide solution, to liberate the amine, which was purified by crystallization from 65% alcohol. Fine yellowish or reddish-violet needles were obtained, m. p. 251° (corr.); yield 70%; bluish-violet fluorescence in alcoholic solution.

Anal. Calcd. for $C_{14}H_{13}N_3S$: C, 65.88; H, 5.13. Pound: C, 6.5.47, 65.63; H, 5.25, 5.21.

2-(*m*-Aminophenyl)-5-methyl-6-aminobenzothiazole.—Attempts to prepare this by reduction of the 2-(m-nitrophenyl) derivative, in the same way as the o-aminophenyl isomer, were unsuccessful, for no product of satisfactory purity could be isolated.

2-(*p*-Aminophenyl)-5-methyl-6-aminobenzothiazole.—When the 2-(*p*-nitrophenyl)-5-methyl-6-(p-nitrobenzalamino)-benzothiazole was similarly reduced with tin and hydrochloric acid, and the crude amine crystallized from 50% alcohol, orange-yellow or greenish-yellow needles were obtained, m. p. 255.5° (corr.); purplish fluorescence in alcoholic solution

Anal. Calcd. for $C_{14}H_{13}N_3S$: C, 65.88; H, 5.09. Found: C, 65.98; H, 5.22.

In the course of the reaction, therefore, the *p*-nitrobenzalamino group was hydrolyzed.

Preparation of a Columbia Yellow Dye from **2-(*o*-Aminophenyl)-5-methyl-6-aminobenzothiazole.**—Some of this thiazole was sulfonated and an aqueous solution of the sodium sulfonate was oxidized with a freshly prepared sodium hypochlorite solution, to obtain a dye of Columbia Yellow (Colour Index No. 814) type. Analysis of the black amorphous product gave figures which indicated that it was probably a mixture of the di- and tetra-sulfo acids.

Anal. Calcd. for $C_{28}H_{20}N_6S_2(SO_3H)_2$: *C*, 50.45; H, 3.34. For $C_{28}H_{18}N_6S_2(SO_3H)_4$: C, 40.67; H, 2.66. Found: C, 46.02; H, 3.33.

It dyed unmordanted unbleached cotton a deep orange-tan, of approximately the same fastness as other dyes of this type. Diazotizing and coupling experiments with β-naphthol led to the conclusion that the dye still retained free amino groups and that probably only the amino groups on the 2-phenyl participated in the formation of the Columbia Yellow dye. The azo dyes so produced were likewise direct dyes for cotton.

Preparation of a Columbia Yellow Dye from **2-(*p*-Aminophenyl)-6-aminotoluthiazole.**—The thiazole (2.5 *g.)* was heated for fifteen hours at 75–85' with a mixture of 20 cc. of concentrated and 25 g. of fuming (50%) sulfuric acid. The solution was poured upon cracked ice, the precipitate collected, dissolved in ammonium hydroxide solution, the solution reprecipitated by hydrochloric acid, this solution and precipitation repeated once or twice and the product dried at 120°.

Anal. Calcd. for $C_{14}H_{12}N_3S(SO_3H)$: C, 50.14; H, 3.88; S, 19.16. For $C_{14}H_{11}N_3S(SO_3H)_2$: C, 40.48; H, 3.13; S, 23.13. Found: C, 41.10, 40.83; H, 3.82, 3.94; S, 19.16, 20.5.

The product is hence a mixture of the mono- and di-sulfonic acids.

It was dissolved in sodium carbonate solution, and mixed with a freshly prepared sodium hypochlorite solution. The solution rapidly turned dark red and, after standing for twenty-four hours, was precipitated by the addition of concentrated hydrochloric acid. The precipitate was collected, dissolved in ammonium hydroxide solution and reprecipitated with hydrochloric acid, then dissolved in water and reprecipitated with concentrated hydrochloric acid, and finally dissolved in water and the solution evaporated on the water-bath. The dye was left as a lustrous black solid.

Anal. Calcd. for $C_{28}H_{20}N_6S_2(SO_3H)_2$: C, 50.45; H, 3.34. For $C_{28}H_{18}N_6S_2(SO_3H)_4$: C, 40.67; H, 2.66. Found: C, 44.90; H, 2.63.

The product was therefore a mixture of di- and tetra-sulfo acids. Its tinctorial properties, as well as its behavior when diazotized and coupled with β-naphthol, were much the same as those stated for the dye from the 2-(*o*-aminophenyl) isomer, except that the dyeings with the latter were of lighter shade.

2-(*o,p*-Diaminophenyl)-5-methyl-6-aminobenzothiazole, secured by reduction of the dinitrophenyl compound in similar manner, crystallized from 50% alcohol in fine orange needles, m. p. 285.5°; yield, 70%; sky-blue fluorescence in alcoholic solution.

Anal. Calcd. for $C_{14}H_{14}N_4S$: C, 62.22; H, 5.18. Found: C, 62.11; H. 5.36.

An attempt to prepare a **thiosulfuric** acid of **2,4-diaminotoluene,** by the process used for the preparation of the 2,5-diaminotoluene-4-thiosulfuric acid, proved unsuccessful.

Summary

1. A method for the preparation of 2,5-diaminotoluene-4-thiosulfuric acid is described. A potentiometric titration of this acid shows its ionization constant to be 5.56×10^{-6} at 25°.

2. Condensation of this acid with nitrobenzaldehydes gives the corresponding 2-nitrophenylaminotoluthiazole, except in the case of the *p*-nitrobenzaldehyde, when the thiazole obtained carries also a *p*-nitrobenzal group on the 6-amino.

3. Certain of these nitro derivatives were reduced to the corresponding amines, and with some of the latter preliminary studies were made of their conversion into dyes of Columbia Yellow type.

NEW YORK, N. Y.

[Contribution from the Chemical Laboratory of the Washington Square College of New York University]

STUDIES IN THE DIARYL ACYL HYDRAZINE SERIES. II. SALT FORMATION IN THE BENZIDINE AND SEMIDINE REARRANGEMENTS

By John J. Ritter and Frank O. Ritter

Received November 12, 1930 Published February 9, 1931

In a previous paper[1] the authors described several unsymmetrical diaryl acetyl hydrazines, with a method for determining their structures based upon reduction with phenylhydrazine. The present communication treats of additional new members of this series, the determination of their structures by oxidation with potassium dichromate in glacial acetic acid solution, and the bearing of this work upon the problem of salt formation in the benzidine and semidine rearrangements.

The oxidation of diaryl acetyl hydrazines has been investigated by Goldschmidt and Euler,[2] who reported the formation of tetrazanes by the oxidation of mono-acetylhydrazobenzene and mono-acetylhydrazo-*p*-toluene in benzene solution with lead dioxide. We have carried out the oxidation of the latter hydrazo compounds and also those described in our previous paper[1] with potassium dichromate in glacial acetic acid at ordinary temperature, and have found that tetrazanes are not formed under these conditions in any case. Two kinds of behavior on oxidation were shown by the acetylhydrazo compounds examined by us. All of the mono-acetylhydrazines previously identified by phenylhydrazine reduction[1] were oxidized with dichromate and were found to divide themselves with reference to behavior on oxidation into two series. The N-acetyl[3] derivatives were oxidized in all cases to the corresponding azo compounds, while the N′-derivatives gave brilliant, intensely colored red or violet solutions from which highly colored crystalline products were isolated.

The production of the colored oxidation products appears to depend upon the presence of the group NH—, since the oxidation of mono-acetylhydrazo-*p*-toluene was found to yield, like the N-acetyl derivatives of the unsymmetrical members studied, the corresponding azo compound. The colored oxidation product derived from mono-acetylhydrazobenzene is under investigation in this Laboratory, and its structure has been established with some certainty. The oxidation of the N-derivatives probably takes place through the steps

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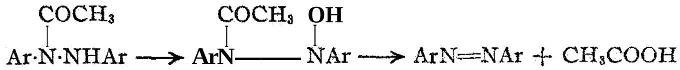
[1] John J. Ritter and Frank O. Ritter, This Journal, 52, 2815 (1930).

[2] Goldschmidt and Euler, *Ber.*, 55, 616 (1922).

[3] N designates the nitrogen atom attached directly to the unsubstituted benzene nucleus, N′, the nitrogen atom in direct union with the nucleus carrying a substituent group.

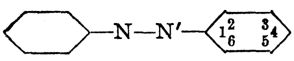


$$Ar\cdot\overset{COCH_3}{N}\cdot NHAr \longrightarrow Ar\overset{COCH_3}{N}—\overset{OH}{N}Ar \longrightarrow ArN{=}NAr + CH_3COOH$$

Having discovered this relationship between structure and behavior on oxidation in those cases where the structures were already determined by phenylhydrazine reduction, we were able to extend it to the determination of the structures of the compounds described in this paper, since each member studied had a *p*-substituent in one nucleus. We have in this way determined the structures of the two isomeric mono-acetyl-*p*-iodohydrazobenzenes, of the single acetyl derivative of *p*-acetoxyhydrazobenzene, which is the N-derivative, of the single mono-acetyl-*p*-carboxyhydrazobenzene, which is also the N-derivative, and of the single mono-acetylbenzenehydrazo-*p*-phenetole, which proved to be the N′-derivative.

The subjoined table summarizes the mono-acetyl hydrazines studied in this and in our previous paper, with the findings as to structure

TABLE I



Substituent group	Position	CH_3CO- attachment	Method of structure-determination	M. p. (corr.), °C.
CH_3	2	N	Red.	78
CH_3	4	N′	Ox. + red.	140–141
CH_3	4	N	Ox. + red.	124
Cl	4	N′	Ox. + red.	111–112
Cl	4	N	Ox. + red.	123–124
Br	4	N′	Ox. + red.	83
Br	4	N	Ox. + red.	117–118
I	4	N′	Ox.	156–157
I	4	N	Ox.	135–136
COOH	4	N	Ox.	207–208
$OCOCH_3$	4	N	Ox.	105–106
OC_2H_5	4	N′	Ox.	108

The symbol "Ox." signifies dichromate oxidation, and "Red.," phenylhydrazine reduction.

The formation of highly colored products on oxidation of the mono-acetylhydrazo compounds appeared, superficially, to bear a relationship to the behavior of certain hydrazo compounds on treatment with mineral acids. Jacobson and Kunz[4] reported the significant fact that *p*-acetamidohydrazobenzene in acid solution became deep blue in color. We have noticed that other hydrazo compounds behave in this manner. Hydrazobenzene, hydrazo-p-phenetole, *p*-methyl-, *p*-chloro-, *p*-bromo- and *p*-iodohydrazobenzene suspended in 10% hydrochloric acid at room temperature, and then exposed to the air for several days, yield blue or violet solutions.

[4] Jacobson and Kunz, *Ann.*, 303, 363 (1898).

The formation of these colored products is undoubtedly caused by air oxidation of the original unrearranged products, since hydrazobenzene, even after the development of color when treated in this manner, contains no detectable amount of benzidine. A solution containing the rearranged products of hydrazobenzene developed no color when similarly treated. The colors can be developed in much shorter time by the addition of hydrogen peroxide.

The oxidation of the hydrazo compounds in the presence of hydrochloric acid, furthermore, was found to be quite parallel with the oxidation of their acetyl derivatives by potassium dichromate; the hydrazo compounds which yielded N-acetyl derivatives were found to give brown solutions on air oxidation, presumably representing the formation of the corresponding azo compounds, while those which gave the N′-acetyl derivatives were readily oxidized to deep red or violet colored products. This behavior is most readily explained by assuming that the hydrazo compounds in acid solution form mono salts, which may involve the N- or N′-atom, and oxidize to new colored substances on the one hand, or to the azo compounds, on the other, depending upon the nitrogen atom involved in salt formation, in a manner analogous to the behavior of their acetyl derivatives. The formation of mono salts in the hydrazo series is in harmony with the fact that hydrazine and many of its simple derivatives function chiefly as mono-acid bases. Acylation and salt formation of amines, furthermore, appear in the present work to be quite parallel, as in the previously reported cases of phenylhydrazine[6] and methylhydrazine.[6]

It may therefore be said with some assurance that some of the unsymmetrical hydrazo compounds studied by us yield only one mono salt when treated with strong acids, while others yield two isomeric mono salts in approximately equal amounts.

Consideration of the products of rearrangement of the seventy-eight hydrazo compounds described by Jacobson[7] reveals the interesting fact that they show a marked tendency to yield exclusively semidines on the one hand, or diphenyloids on the other. There appear to be only eight outstanding exceptions to this rule, comprising a group in which each member yields both diphenyloids and semidines simultaneously, and in nearly equal amounts; among the eight exceptions occur the members each of which this research has shown to yield two isomeric acetyl derivatives in nearly equal amounts. Thus, benzenehydrazo-+-toluene, *p*-chloro-, P-bromo- and *p*-iodohydrazobenzenes each yield both diphenyloids and semidines. These facts suggest that the salts of hydrazo compounds are involved in their rearrangement, and, further, that the formation of a

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[5] E. Fischer, Ann., **190**, 131 (1878).

[6] Von Brüning, *ibid.*, **253**, 10, 12 (1889).

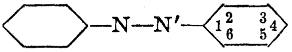
[7] Jacobson, *ihid.*, **428**, 90–97 (1922).

salt of definite structure precedes the formation of a definite type of rearrangement product. Examination of Jacobson's[7] summary of the rearrangement of the various symmetrical hydrazo compounds (the structures of whose mono salts are known), supplemented by our own observations as to the structures of the salts of various unsymmetrical hydrazo compounds, discloses the following interesting relationship: when salt formation takes place on a nitrogen atom attached to an aryl nucleus in which the *p*-position is open, diphenyloids result, while semidines are formed when the salt in question involves a nitrogen atom attached to a nucleus carrying a *p*-substituent.

Considering the problem from this point of view, it seems that the type of rearranged product is determined by the structure of its mono salt. The tendency to rearrange to one type is so strong that it will often occur even with displacement of para groups already in the ring. However, the character and position of groups (other than para) undoubtedly have an influence, and determine the details within the two main types. It is in the latter sense that Jacobson's[7] rules apply.

It is planned to study other members of the group to determine whether their behavior on acetylation and on oxidation in acid solution is in harmony with the above generalizations. Table II illustrates the relationship between salt structure and type of rearrangement undergone by those hydrazo compounds the structure of whose mono salts is established by this investigation.

TABLE II



Substituent group	Position	Salt formation on	Type of rearrangement
COOH	(4)	N	Diphenyloid
$OCOCH_3$	(4)	N	Diphenyloid
CH_3	(2)	N	Diphenyloid
OC_2H_5	(4)	N'	Semidine
Cl	(4)	N + N'	Diphenyloid + semidine
Br	(4)	N + N'	Diphenyloid + semidine
I	(4)	N + N'	Diphenyloid + semidine
CH_3	(4)	N + N'	Diphenyloid + semidine

By extending this relationship to benzenehydrazo-p-toluene, *p*-chloro-, *p*-bromo and *p*-iodohydrazobenzenes, it may be concluded that diphenyloid rearrangement is preceded by formation of the N-salts, and semidine rearrangement by the formation of N'-salts.

A criticism of the hypothesis of Frantzen and Furst,[8] may also be offered. These authors suggest that the benzidine and semidine rearrangements involve the formation of mono salts which then separate into the corresponding amine and halamine

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[8] Frantzen and Furst, *Ann.*, **412**, 19 (1917).

$$\mathrm{ArNH_2Cl{-}NHAr'} \longrightarrow \mathrm{ArNHCl + Ar'NH_2}$$

The latter are supposed to react, either as such or with intermediate rearrangement of the halamine to the o- or p-quinol form, to yield the final rearrangement products. Jacobson[9] has pointed out that this scheme does not harmonize with the "maintenance of the aryl combination" in the rearranged products, *i. e.*, the fact that the products of rearrangement always contain the original combination of aryl groups. He says that salt formation and breakdown in only one sense must be assumed in order that the aryl combination remain fixed. Our work has shown that this assumption cannot be made in those cases where the formation of two acetyl derivatives shows the ability of the compound in question to form two different salts. In those cases where only one acetyl derivative is formed, and hence only one salt, the hypothesis is on surer ground. Here only one type of amine and halamine is possible and the aryl combination is maintained.

Experimental Part

The preparation of the azo compounds, their reduction and the formation and separation of their acetyl derivatives were carried out as outlined in an earlier communication.[1] The experimental details of these operations will therefore be omitted in the present report.

Azo Compounds.—p-Iodoazobenzene, m. p. 105°, in agreement with Noelting and Werner;[10] *p*-carboxyazobenzene, made by condensation of *p*-aminoethylbenzoate with nitrosobenzene followed by saponification of the ester with alcoholic potassium hydroxide, m. p. 237–238° (corr.), in agreement with Jacobson and Steinbrenk;[11] *p*-acetoxyazobenzene, m. p. 82–83°. Wallach and Kiepenheuer[12] reported 84–85°; benzeneazo-*p*-phenetole, m. p. 77–78°, in agreement with Jacobson and W. Fischer.[13]

Hydrazo Compounds.—p-Iodohydrazobenzene, m. p. 105–106°, in agreement with Noelting and Werner;[10] *p*-carboxyhydrazobenzene, m. p. 192–193° (corr.), in agreement with Jacobson and Steinbrenk;[11] *p*-acetoxyhydrazobenzene, pearly plates from 95% alcohol, m. p. 117–118° (corr.).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: N, 11.57. Found: (micro Dumas) N, 11.14.

Acetylhydrazo Compounds.—The more important characteristics of the new acetyl compounds are listed below. N-Acetyl-p-iodohydrazobenzene, clusters of needles from 95% alcohol, m. p. 135–136° (corr.).

Anal. Calcd. for $C_{14}H_{13}N_2OI$: N, 7.95. Found: (micro Dumas) N, 7.45.

N′-Acetyl-*p*-iodohydrazobenzene, prisms from 95% alcohol, m. p. 156–157° (corr.).

Anal. Calcd. for $C_{14}H_{13}N_2OI$: N, 7.95. Found: (micro Dumas) N, 7.89.

N-Acetyl-p-carboxyhydrazobenzene, needles from 95% alcohol, m. p. 207–208° (corr.).

Anal. Calcd. for $C_{15}H_{14}N_2O_3$: N, 10.37. Found: (micro Dumas) N, 10.70.

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[9] Jacobson, *Ann.*, 428, 118 (1922).

[10] Noelting and Werner, *Ber.*, 23, 3255 (1890).

[11] Jacobson and Steinbrenk, *Ann.*, 303, 384 (1898).

[12] Wallach and Kiepenheuer, *Ber.*, 14, 2617 (1881).

[13] Jacobson and W. Fischer, *ibid.*, 25, 994 (1892).

N'-Acetyl-benzenehydrazo-*p*-phenetole.—This compound was difficult to prepare from the corresponding hydrazo compound because the latter underwent self-oxidation–reduction in the presence of acetic anhydride. The acetyl derivative was obtained in good yield by reduction of benzeneazo-p-phenetole with zinc dust and glacial acetic acid in acetic anhydride solution; colorless nodules composed of fine needles, m. p. 108".

Anal . Calcd. for $C_{16}H_{18}N_2O_2$: N, 10.37. Found: (micro Dumas) N, 10.54.

N-Acetyl-*p*-acetoxyhydrazobenzene, fine colorless needles from alcohol, m. p. 105–106°.

Anal. Calcd. for $C_{16}H_{16}N_2O_3$: N, 9.86. Found: (micro Dumas) N, 9.22.

Oxidation of the Acetyl Derivatives.—The acetyl derivatives (one mole) were dissolved in glacial acetic acid to form a 10–15% solution, and then shaken for twenty-four hours on a mechanical bottle-shaker with finely ground potassium dichromate (0.66 mole). The N-derivatives yielded deep violet solutions immediately under these conditions, although the completed reaction required ten or more hours. The N-derivatives yielded brown solutions. The solutions were filtered after oxidation to remove any unused potassium dichromate, and then diluted with about five volumes of cold water. After standing overnight, the oxidation products appeared as precipitates which were separated by filtration. The brown solutions yielded in each case the corresponding azo compounds, which were identified by their melting points, and by comparison with authentic samples. The violet solutions yielded dark red crystalline solids. The product so obtained from acetylhydrazobenzene has been recrystallized from petroleum ether and then from alcohol in large plates of dark red color melting at 163° (corr.).

Oxidation of the Wydrazo Compounds.—Small quantities (0.1–0.2 g.) of the hydrazo compounds were suspended in 10% hydrochloric acid at room temperature, and allowed to stand exposed to the air for several days. Those which were found to yield N'-acetyl derivatives were found also to impart a deep violet color to the acid solutions, while those yielding N-acetyl derivatives became brown in color. Benzenehydrazo-*p*-toluene, *p*-chloro-, p-bromo- and p-iodohydrazobenzenes gave violet solutions in which the brown oxidation products were presumably formed also, although their presence could not be detected visually because of the intense violet color of the solutions. *p*-Acetoxy-and p-carboxyhydrazobenzenes, under the same conditions, gave orange-colored solutions. To make certain that the colored products resulted from the oxidation of the hydrazo compounds and not their products of rearrangement, the following experiment was performed: 0.1–0.2 g. of hydrazobenzene was boiled for five minutes with 5 cc. of concentrated hydrochloric acid. A clear solution was obtained, which was diluted with water until the acid concentration was approximately 10%. The solution was exposed to the air for several days, and remained colorless. Further work upon the isolation and identification of these colored air-oxidation products is in progress.

Summary

1. Several new diaryl acyl hydrazines have been prepared.
2. A method for their identification by means of oxidation has been described.
3. The formation of highly colored products from hydrazo compounds in contact with acids has been shown to be caused by air oxidation.
4. A relationship between the salt-forming properties of the nitrogen atoms in hydrazo compounds and their rearrangement in acid solution has been established.
5. The oxidation of hydrazo compounds in acid solution has also been

investigated and correlated with the oxidation of their acetyl derivatives. The phenomena observed have been found to have intimate bearing upon the benzidine and semidine rearrangements.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE REDUCTION OF TRIPHENYLMETHANE DYES AND RELATED SUBSTANCES WITH THE FORMATION OF FREE RADICALS

BY JAMES B. CONANT AND NEWELL M. BIGELOW

RECEIVED NOVEMBER 15, 1930 PUBLISHED FEBRUARY 9, 1931

The work of Clark and collaborators[1] has shown that the reduction of many different dyes by soluble reducing agents is a process analogous to the reduction of quinones in that the leuco compound and the dyestuff form a mobile oxidation–reduction system. The reduction and reoxidation occur rapidly at room temperature even in dilute solution and characteristic and significant oxidation potentials may be measured. The indigoids, many anthraquinone dyes, indophenols, indamines and methylene blue are all of this type. The reduction of azo dyes and triphenylmethane dyes is of a different sort; here, the reduction product (or products) are not rapidly reoxidized and no significant oxidation–reduction potentials can be measured by the usual methods. An examination of the behavior of the azo dyes has already been made in this Laboratory;[2] the present paper deals with the unraveling of the chemical reactions involved in the action of soluble reducing agents on triphenyl methane dyes; a quantitative study of certain of these reactions will be included in a later paper.

The color bases of the triphenylmethane dyes are substituted triphenylcarbinols; the dyes themselves are salts which are related to the halochromic salts of triphenylcarbinol. The exact method of formulating the structure of the colored positive ion of the triphenylmethane dyes and that of the halochromic salts has been the subject of much discussion. We shall not attempt to take sides in this controversy; the distinction between triphenylmethyl sulfate and malachite green appears to be one of degree rather than of kind as far as our work is concerned. It was shown some years ago,[3] that the halochromic salts of triphenylcarbinol and related substances are reduced by powerful reducing agents in appropriate solutions with the formation of the corresponding free radical (*e.g.*, triphenylmethyl). The free radical and halochromic salt form a mobile oxidation–

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[1] W. M. Clark and co-workers, "Studies in Oxidation–Reduction." Reprints I-X Hygienic Laboratory Bulletin No. 151.

[2] Conant and Pratt, THIS JOURNAL, 48, 2468 (1926).

[3] Conant, Small and Taylor, *ibid.*, 47, 1959 (1925).

reduction system whose potential may be measured in the usual way. A similar situation would be expected in regard to the cations of the triphenylmethane dyes except that the resulting free radical would be expected to be even more unstable in acid solution than triphenylmethyl. (The sensitivity of free radicals toward acids is well known and particularly pronounced when "positive" groups like methoxyl are present in the molecule.) These expectations have been confirmed by experiment, and we may write the following general reactions in which R^+ stands for the positive ion of the dye and M^{++} stands for a soluble reducing ion such as titanous, vanadous or chromous.

(1) $\underset{\text{cation}}{R^+} \ 4 \ M^{++} \rightleftharpoons \underset{\text{free radical}}{R—} + M^{+++}$ (fast, reversible)

(2) $2R— \rightleftharpoons \underset{\text{"ethane"}}{R—R}$ (fast, reversible or irreversible depending on nature of R)

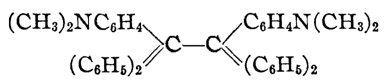
(3) $2R— + H^+ \longrightarrow \underset{\text{"methane"}}{RH} + R^+$ (irreversible)

(4) $2R— \longrightarrow \underset{\text{(Chichibabin compounds)}}{R_2}$ (irreversiblecatalyzed by acid)

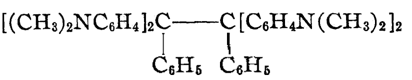
The factors influencing the composition of the equilibrium mixture in Reaction 1 have been outlined in a previous paper;[3] they include in addition to the oxidation–reduction potentials of the system R+, R and M^{++}, M^{+++}, the hydrogen-ion activity and water activity of the medium, provided the reaction $R^+ + H_2O$ $ROH + H^+$ is mobile. Since Reactions **3** and 4 are irreversible and since the product of Reaction 2 may be very insoluble in the medium employed, the overall reaction may go rapidly to completion even if a very small amount of product is formed in the first reaction.

We have established the validity of the foregoing account of the reduction of triphenylmethane dyes by isolating the products of Reactions 2, **3** and 4 in the case of malachite green (a typical dye) and *p*-dimethylaminotriphenylcarbinol. The latter may be regarded as a transition compound between the dyes and triphenylcarbinol. Titanous, vanadous and chromous salts were employed as reducing agents.

In order to isolate the associated free radical (the "ethane") it is necessary to take advantage of its relative insolubility in aqueous solutions of *P*H value of about **3**; it is also necessary to avoid the irreversible decompositions which are brought about by strong acids (Reaction **3**). *Sym.-p,p*-tetramethyldiaminohexaphenylethane (I) and *p,p,p',p'*-octamethyltetraminohexaphenylethane (II) have been isolated as brown amorphous powders by the reduction of the corresponding chlorides in acetic acid and precipitation with water in the presence of sodium acetate. Extreme pre-



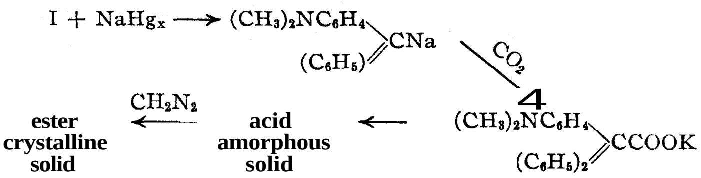
I



$[(CH_3)_2NC_6H_4]_2\underset{C_6H_5}{C}—\underset{C_6H_5}{C}[C_6H_4N(CH_3)_2]_2$

II

cautions must be taken in drying and handling the compounds. On exposure to a trace of oxygen the dry solids are decomposed with the evolution of formaldehyde. When first prepared in the moist state, the compounds are somewhat more stable. Crystallization was attempted without success and, therefore, no analyses can be reported. In spite of this the nature of the substances was established beyond question. Like all derivatives of hexaphenylethane, in solution they absorb oxygen very rapidly; as high as 89% of the amount corresponding to the formation of a peroxide was absorbed by a solution of the crude dried material. In the case of the diamino compound (I) a crystalline peroxide was isolated and analyzed. In this case also the substituted acetic acid could be obtained by the following series of reactions:



The sodium methide is unstable; on standing in ether suspension the characteristic color disappears and the corresponding methane is formed. This replacement of sodium by hydrogen may be the result either of the action of the ether (as in the case of sodium methyl) or some reaction involving one of the methyl groups on the nitrogen atom. This reaction is so rapid in the case of the ethane from malachite green (II) that only a fleeting color can be observed when an ethereal solution is shaken with sodium amalgam with the usual precautions; the solution was then found to contain the corresponding hydrogen compound (*p*, *p'*-tetramethyldiaminotriphenylmethane). Both ethanes (I and II) dissolve in neutral organic solvents with the formation of an orange solution indicating considerable dissociation into the free radicals. The significant difference in color between the solution of the free radical and the corresponding positive ion (cation of malachite green) has been discussed by Wieland, who prepared for this comparison solutions of the free radicals corresponding to a number of triphenylmethane dyes by the thermal decomposition[4] of azo compounds.

The decomposition of these dissociable ethanes by acid is easily demonstrated. For example, glacial acetic solutions of both ethanes slowly lose their oxygen-absorbing capacity. In concentrated hydrochloric acid both ethanes are at once decomposed. The nature of the decomposition product depends on the conditions; in a weakly acidic medium such as glacial acetic acid, the methane and the corresponding positive ion are formed; since the latter is, of course, further reduced (Equation 1), the prolonged action of reducing agents in acetic acid solutions yields only the substituted

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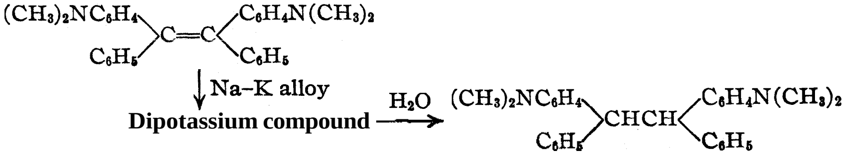
[4] Wieland, Popper and Seefried, *Ber.*, 55, 1816 (1922).

triphenylmethane, which is regarded as the leuco compound (Equations 1 and 3). The distinction between such leuco compounds and those corresponding to indigo and methylene blue is obvious; the free radical (or the corresponding ethane) should be regarded as the real leuco compound in the case of the triphenylmethane dyes. As would be expected, reducing agents such as zinc and acid reduce the ethanes to the corresponding methanes.

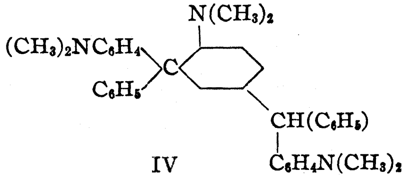
The action of concentrated hydrochloric acid on the free radicals appears to cause the irreversible formation of a dimer, isomeric with the dissociable ethane. Since this phenomenon is similar to the formation of p-benzhydryltetraphenylmethane from triphenylmethyl (a reaction first elucidated by Chichibabin), we shall designate these dimers as Chichibabin compounds. They were obtained by the use of chromous chloride in concentrated hydrochloric acid: analysis and molecular weight showed them to be isomeric with the dissociable ethanes; they are not affected by acids, oxygen or sodium–potassium alloy. Their structure has not been established, nor have they been isolated from the tarry material formed by the action of concentrated hydrochloric acid on the dissociable ethanes. Nevertheless, their mode of formation and empirical formulas show them to be dimolecular reduction products of the cations in question.

We have included in our study the mono-*p*-dimethylamino derivative of diphenyicarbinol. This substance is reduced in acetone solution containing hydrochloric acid by chromous chloride. The products are two isomeric dimers; the lower-melting and more soluble substance has been shown to be *p,p'*-tetramethyldiaminotetraphenylethane by its synthesis from the well-known ethylene by the reactions



III

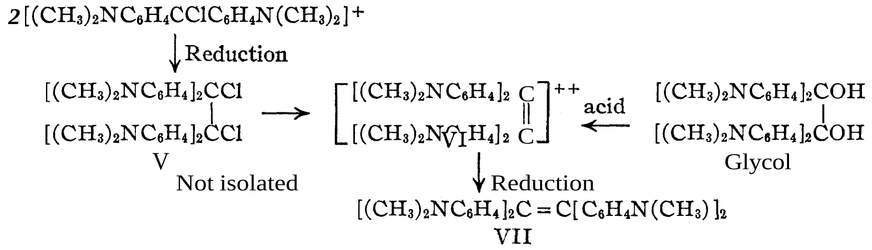
The constitution of the higher-melting isomer has not been established; presumably it is a Chichibabin compound such as represented by formula IV, though it might be a diastereoisomeride of III. The formation of both isomers probably proceeds through the formation of the same free radical.



IV

In this case the normal association produces a tetraphenyl compound, and the reaction is therefore irreversible like the Chichibabin reaction.

The action of vanadous chloride or chromous chloride on the keto chloride of Michler's ketone (*p,p′*-tetramethyldiaminodiphenyl ketone) is similar to the reduction of the salts of the diphenylcarbinols. The keto chloride which is bright blue is undoubtedly a compound in which one chlorine is in the ionic condition and the cation has a structure similar to that of the triphenylmethane dyes (in regard to which there are many opinions.) On reduction one would expect to obtain the corresponding dichloroethane (V); the actual product, however, is the corresponding ethylene (VII). The steps involved in reaction appear to involve the initial formation of the dichloride V and its ionization to the corresponding salt.[5] This salt on reduction gives the ethylene, as we proved in a separate experiment



$$2[(CH_3)_2NC_6H_4CClC_6H_4N(CH_3)_2]^+$$

$$\Big\downarrow \text{Reduction}$$

$$\underset{\substack{\text{V}\\\text{Not isolated}}}{\begin{array}{c}[(CH_3)_2NC_6H_4]_2CCl\\ |\\ [(CH_3)_2NC_6H_4]_2CCl\end{array}} \longrightarrow \underset{\text{VI}}{\left[\begin{array}{c}[(CH_3)_2NC_6H_4]_2\ C\\ \|\\ [(CH_3)_2NC_6H_4]_2\ C\end{array}\right]^{++}} \xleftarrow{\text{acid}} \underset{\text{Glycol}}{\begin{array}{c}[(CH_3)_2NC_6H_4]_2COH\\ |\\ [(CH_3)_2NC_6H_4]_2COH\end{array}}$$

$$\Big\downarrow \text{Reduction}$$

$$\underset{\text{VII}}{[(CH_3)_2NC_6H_4]_2C = C[C_6H_4N(CH_3)]_2}$$

starting with the corresponding glycol. The mobility of the system VI–VII will be investigated by electrochemical methods.

Finally it may be noted that aryl-alkyl-carbinols may also undergo dimolecular reduction in acid solution with chromous chloride. Thus, *p*-dimethylaminophenylisopropylcarbinol is reduced to two isomeric dimers. Presumably one of these is *p,p′*-tetramethyldiaminodiisopropylethane and the other a Chichibabin hydrocarbon. However, their structure has not been elucidated.

Experimental

Preliminary Experiments on Reductions of *p*-Dimethylaminotriphenylcarbinol.—Six-tenths of a gram of *p*-dimethylaminotriphenylcarbinol was dissolved in the chosen solvent in a small flask directly joined to a larger one. In the larger chamber were placed 15 cc. of bromobenzene, 15 g. of crushed ice and 50 cc. of an aqueous solution containing 5.0 g. of sodium acetate and sodium hydroxide in quantity not quite equivalent to the acid in the reducing mixture. The system was swept with nitrogen, and the reducing agent was added through a stopcock in the neck of the smaller chamber. When the reduction was complete, judging from the disappearance of the halochromic color, the reduction mixture was allowed to run into the larger chamber; the apparatus was shaken vigorously until all of the bromobenzene was drawn from the bottom stopcock into a graduated test-tube filled with freshly distilled water; the organic layer displaced the water and did not come in contact with the air. It was found impossible to drain off all of the bromobenzene without including some of the aqueous layer; hence two-thirds of it was used, and the remainder allowed for in the calculation of the theoretical absorption.

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[5] *Cf.* Madelung, *Ber.*, 60, 2469 (1927); Wizinger, *ibid.*, 60, 1377 (1927).

Experiment showed that the "blank" absorption, as well as the errors due to deviations from the standard temperature and pressure, were within the limit of experimental error. These factors were accordingly overlooked.

The results of the preliminary reductions are tabulated:

Solvent	Time, min.	Temp., °C.	Absorption, cc.	Per cent. of absorption
15 cc. acetic acid	2	20	13.2	89
15 cc. acetic acid	10	20	11.2	75
15 cc. acetic acid	30	20	12.4	83
15 cc. acetic acid	120	20	9.3	62.5
15 cc. hydrochloric acid	2	30*	0	0
10 cc. acetone, 5 cc. hydrochloric acid	3	30*	0	0
20 cc. acetic acid, 5 cc. hydrochloric acid	3	0–5	4.2	28
20 cc. acetic acid, 5 cc. hydrochloric acid	6	0–5	4.2	28

* The heat of neutralization raised the temperature of the precipitating mixture to 30°.

Sym.-p,p-**tetramethyldiaminohexaphenylethane.**—Three grams of *p*-di-methylaminotriphenylcarbinol was dissolved in 45 cc. of glacial acetic acid in the large chamber of the reduction apparatus. The system was evacuated and filled with nitrogen; then, against a stream of nitrogen, 20 cc. of 1 N chromous chloride or vanadous chloride was pipetted into the smaller chamber. The system was stoppered and swept again with nitrogen; then the two reagents were mixed by tilting the apparatus. The deep red color of the carbinol salt disappeared in about thirty seconds, the apparatus being meanwhile shaken vigorously. Nitrogen was then forced into the system, and the mixture was allowed to flow from the bottom stopcock into a freshly boiled and chilled solution of 10 g. of sodium acetate in 800 cc. of water. On dilution, a flesh-colored amorphous precipitate of *sym.-p,p'*-tetramethyldiaminohexaphenylethane appeared. The suspension was stirred for a few seconds, and was then filtered by suction as rapidly as possible. The filter cake was washed rapidly, first with water and then dilute ammonia; it was transferred as rapidly as possible to a drying pistol. More than a few moments' exposure of the precipitate to the air caused the formation of a bright red crust of oxidized product to appear on its surface. Calcium chloride was used as the drying agent; the pistol was evacuated, filled with nitrogen and re-evacuated. About thirty-six hours were necessary to dry the precipitate thoroughly.

The dried product was a fluffy flesh-colored powder, colored bright red on its surface by a crust of oxidized material. On even momentary exposure to air it decomposed instantly to a deep red tar, evolving heat and an odor of formaldehyde. The oxygen absorption of the dried amorphous powder when dissolved in bromobenzene was 70–85% of the theoretical amount. Manipulations of the solid were in carbon dioxide. The apparent molecular weight of this material was determined in *p*-chlorotoluene (freezing point) and found to be 458–507 as compared with 572.5 for the ethane.

The attempts to crystallize the free radical were unsuccessful. The crude product was found to be readily soluble in ether and benzene. When alcohol was added to an ethereal solution of the compound, the solution became deep red in color. A red solid crystallized from this mixture; it was not the pure ethane, however, since its oxygen capacity was only half of the theoretical amount. The free radical was insoluble in petroleum ether and could be precipitated in an amorphous state when this solvent was added to an ethereal solution, but no crystalline product could be obtained. The ethane could not be crystallized from a mixture of acetone and water. When an ethereal solution of the ethane was evaporated to dryness in *vacuo,* the product was a brittle froth which filled the entire system.

Decomposition of the Ethane in Acid Solutions.—Small weighed bulb tubes with constricted necks were swept with carbon dioxide, stoppered and weighed. The stoppers were tied to the tubes to prevent mixing. The weighed tubes were transferred in an atmosphere of carbon dioxide and charged with 0.15–0.20 g. samples of the ethane. They were stoppered and reweighed. A small separatory funnel with a side tube just below the stopcock was fastened in the mouth of a bulb tube with a rubber stopper; the tube was at once evacuated and filled with nitrogen through the side tube. Five cubic centimeters of the chosen solvent was next drawn into the tube under a slightly diminished pressure. The bulb tube was sealed off at the constriction; just before the tube was closed off, the excess pressure in the bulb was relieved through the side arm of the separatory funnel. Bulbs so prepared were kept for varying lengths of time, and were then broken in the absorption apparatus. The amount of free radical left unattacked was calculated from the volume of oxygen absorbed. This method is not sufficiently accurate to warrant the assignment of quantitative significance to the results; it merely indicates the relative rates of decompositiori in acids of varying strength.

IN GLACIAL ACETIC ACID

Temperature 18°; pressure, 761 mm.

Ethane, g.	Time, minutes	Absorption, cc.	Absorption, %
0.29	0	7.6	63.5
.24	35	5.7	57
.47	120	4.3	22

DECOMPOSITION IN ONE MOLAR PYRIDINE IN GLACIAL ACETIC ACID

Temperature, 20°; pressure, 761 mm.

0.29	0	7.6	62
.23	30	5.7	59
.21	90	4.9	55
.23	360	3.6	37

p-Dimethylaminotriphenylmethyl Peroxide.—When an ethereal solution of *sym.*-p,p'-tetramethyldiaminohexaphenylethane was exposed to the air, its color decreased momentarily, and then gradually turned to a deep red. The fine light brown crystals which appeared on the sides of the container were filtered off and washed with acetone. They were insoluble in all the ordinary low-boiling solvents, and decomposed to a red tar when heated in high-boiling solvents. The crude crystals melted with decomposition at 145–150°, dependent on the rate of heating of the melting point bath. The peroxide dissolved in concentrated hydrochloric acid; the solution, at first light red, rapidly turned deep red, at the same time developing a strong odor of phenol.

Anal. Calcd. for $C_{42}H_{40}O_2N_2$: C, 83.4; H, 6.7. Found: C, 82.2; H, 6.6.

Sodium p-Dimethylaminotriphenylmethide.—Two and one-half grams of *sym.*-p,p'-tetramethyldiaminohexaphenylethane was prepared by the usual procedure. The dry product was transferred in an atmosphere of carbon dioxide to a 100-cc. flask which was then closed with a rubber stopper bearing a straight glass stopcock. The container was swept with nitrogen; then 40 cc. of anhydrous ether and 15 cc. of 1% sodium amalgam was introduced through the stopcock. The flask was shaken by hand. After about one minute the color of the solution faded momentarily; then the bright orange-red color of the sodium salt appeared, and grew rapidly in intensity. The solution was shaken on a machine for four hours, at the end of which time the concentration of the sodium salt had reached its maximum. The solution was now deep orange-red; little or none of the solid methide could be seen in the mixture. If the shaking was continued overnight, the color of the solution disappeared. The resulting colorless ethereal solution, filtered from the amalgam and evaporated, yielded two crystalline products; these were separated by crystallization from a concentrated ethereal solution. The product which remained in solution was identified by a mixed melting point as *p*-dimethylaminotriphenylmethane. The product crystallizing from ethereal solution was a white solid melting at 138°; it was not identified

***p*-Dimethylaminotriphenylacetic** Acid.--Carbon dioxide was admitted to the flask containing the methide; decomposition took place rapidly. The ethereal layer was decanted from the amalgam, and the latter was washed several times with ether The combined ethereal layers were extracted several times with dilute sodium hydroxide, the combined aqueous layers were extracted once with ether. The aqueous solution of the sodium salt was boiled for a few minutes to expel the ether; it was then cooled and made exactly neutral with dilute hydrochloric acid, methyl orange being used as the indicator. A thick amorphous precipitate of p-dimethylaminotriphenylacetic acid separated. The precipitate was filtered, washed and dried *in vacuo* over calcium chloride. The crude product weighed 0.64 g., 29% of the theoretical amount. All attempts to crystallize *this* acid were unsuccessful.

Combining Weight with Sodium Hydroxide.—0.1850 g. of the acid neutralized 4.92 cc. of 0.1013 N sodium hydroxide; 0.2004 g. neutralized 5.30 cc. of 0.11113 N sodium hydroxide. Mol. wt. calcd. for $C_{22}H_{21}O_2N$: 331. Found: 371,373

Methyl ***p*-Dimethylaminotriphenylacetate.**—A solution of about 0.18 g. of diazomethane in 25 cc. of anhydrous ether was prepared. To this was added a solution of 0.46 g. of p-dimethylaminotriphenylacetic acid in 15 cc. of absolute methyl alcohol. The solution was allowed to stand for forty-five minutes; then 15 cc. of weakly acidulated water was added to destroy the excess diazomethane. The layers were washed with water, dried with sodium sulfate and concentrated to a volume of 4–5 cc. on a steam-bath. The addition of petroleum ether precipitated the ester in crystalline form. The yield was 0.31 g.; the product, after a second crystallization from the same solvents, melted at 141°.

Anal. Calcd. for $C_{23}H_{23}O_2N$: C, 80.0; H, 6.7. Found: C, 79.9, 80.0; H, 6.7, 7.0.

Molecular Weight, Micro Method.—Sample, 0.0134; camphor, 0.1219; average depression, 13 2. Calcd. for $C_{23}H_{23}O_2N$: 345. Found: 330.

“Chichibabin Product” from **Dimethylaminotriphenylcarbinol.**—A solution of 4.5 g. of p-dimethylaminotriphenylcarbinol in 90 cc. of acetone and 45 cc. of concentrated hydrochloric acid was treated in the absence of air with 25 cc. of 1 N chromous chloride. The solution was allowed to stand at room temperature for twenty-four hours; it was then poured into twice its volume of water and almost neutralized with sodium hydroxide. The mixture, still warm from the neutralization, was extracted several times with benzene. The united benzene layers were washed with water, dried with sodium sulfate and diluted with *n*-butyl alcohol. The benzene was driven off on a steam-bath. Two and six-tenths grams of the crude product separated after a few days' standing. The product, after two more crystallizations from the same solvent, weighed 1.5 g. and melted at 165°. This product dissolved in hydrochloric acid without coloration.

Anal. Calcd. for $C_{42}H_{40}N_2$: C, 88.1; H, 7.0. Found: C, 88.1; H, 6.8.

Molecular Weight, Micro **Method.**—Sample, 0.0132; camphor, 0.1109; average depression, 9 1°. Calcd. for $C_{42}H_{40}N_2$: 672 5. Found: 525.

The Long-Period Reduction of ***p*-Dimethylaminotriphenylcarbinol** with **Chromous** Chloride and **Titanous** Chloride.—Ten cubic centimeters of 1 N chromous chloride was added to a solution of 1.5 g. of p-dimethylaminotriphenylcarbinol in 30 cc. of acetic acid. The solution was allowed to stand for ninety-six hours and was then poured into 400 cc. of 10% sodium acetate solution. A white amorphous precipitate separated. The mixture was extracted with chloroform; the united chloroform layers were dried over sodium sulfate and concentrated. The solution was diluted with isopropyl alcohol and cooled; 0.5 g. of a white crystalline solid separated which was identified by a mixed melting point as p-dimethylaminotriphenylmethane.

One-half gram of p-dimethylaminotriphenylcarbinol and 3 g. of sodium acetate were dissolved in 18 cc. of acetic acid. To this solution 5 cc. of 20% titanous chloride was added in the absence of air. The reaction mixture was allowed to stand for forty-eight hours; it was then poured into 250 cc. of 10% sodium tartrate. The resulting suspension was filtered with suction, dried and recrystallized from benzene–isopropyl alcohol. The crystalline product weighed 0.25 g., 50% of the theoretical amount, and melted at 134°. A sample of the product did not depress the melting point of a sample of *p*-dimethylaminotriphenylmethane.

The Reaction of *p,p'*-Tetramethyldiaminohexaphenylethane with Acetic Acid.—One and seven-tenths grams of *sym.-p,p'*-tetramethyldiaminohexaphenylethane was dissolved in the absence of air in 50 cc. of glacial acetic acid. Solution took place rather slowly, and the solution acquired a deep red color. The solution was allowed to stand for forty-eight hours; it was then poured into 400 cc. of water. A light red precipitate came out; this precipitate was filtered out at once. Crystallization from chloroform–alcohol yielded 0.4 g. of p-dimethylaminotriphenylmethane; the product was identified by a mixed melting point.

The Reaction of *Sym.-p,p'*-Tetramethyldiaminohexaphenylethane with Titanous Chloride.—One and seven-tenths grams of *sym.-p,p'*-tetramethyldiaminohexaphenylethane and 5 g. of sodium acetate were placed in a 50-cc. Erlenmeyer flask. The flask was closed with a one-holed rubber stopper bearing a straight glass stopcock. The flask was swept with nitrogen and evacuated; then 40 cc. of 80% acetic acid and 10 cc. of titanous chloride were drawn into it through the stopcock. The flask was again swept with nitrogen, and was allowed to stand for forty-eight hours. At the end of this time the solution was poured into 300 cc. of 5% sodium tartrate; the resulting suspension was thoroughly extracted with chloroform. The washed and dried chloroform extracts were concentrated and diluted with isopropyl alcohol; on cooling, 1.2 g. of p-dimethylaminotriphenylmethane crystallized. The product was identified by means of a mixed melting point.

***Sym.-p,p',p'',p'''*-Octamethyltetraminohexaphenylethane.**—Two grams of commercial malachite green and 2.0 g. of fused sodium acetate were dissolved in a mixture of 20 cc. of glacial acetic acid and 20 cc. of water. The solution was filtered into the larger chamber of the reduction flask. The system was swept with pure nitrogen; then 20 cc. of 1 N vanadous chloride was pipetted into the smaller chamber against a counter current of nitrogen. The apparatus was again swept with nitrogen; then it was tilted and the two solutions were allowed to mix. The reduction was very rapid. As soon as the deep green color of the solution had disappeared, the lower end of the bottom stopcock was immersed in 200 cc. of freshly boiled and cooled water in which 10 g. of sodium acetate had been dissolved. Nitrogen was blown into the reduction flask, and the reduced solution was forced out of the flask into the sodium acetate solution. The reduction product came out as a light brown amorphous precipitate. The solution was stirred briskly for a few seconds; the precipitate on the surface began to turn green at once. The precipitate was filtered by suction, and washed on the filter with water and very dilute ammonium hydroxide. The moist filter cake, the surface of which was already a bright green, was transferred to a small box made of folded filter paper. The box and its contents were placed directly upon the surface of a layer of calcium chloride in a vacuum desiccator; this was at once evacuated, filled with pure nitrogen and again evacuated to the lowest pressure obtainable. The amorphous free radical was sufficiently dry for ordinary use within twenty-four hours. The procedure outlined above must be followed closely if satisfactory results are to be obtained. Otherwise the product is a brittle black crust, with which very little work can be done.

If the reaction is successful, *sym.-p*-octamethyltetraminohexaphenylethane is obtained as a fluffy amorphous powder, light brown in its interior and bright green on its surface. All manipulations with the radical had to be performed in an atmosphere of carbon dioxide. Exposed to the air, the compound instantly decomposed to a black tar with the evolution of heat and a strong odor of formaldehyde.

Oxygen Absorptions.—In these experiments, the solid ethane was dissolved directly in the chosen solvent. The oxidation product formed a tarry coating over the undissolved ethane; the solubility and the rate of solution of this tar determined the apparent oxygen capacity of the ethane in a given solvent. The first three typical absorptions given below show the varying capacity of the same sample of ethane in different solvents.

Ethane	Solvent	Absorption, cc. (22.5°, 761 mm)	Per cent. absorption
0.16	Bromobenzene	2.0	34
.27	Aniline	5.1	52
.30	Acetic acid	7.5	68
.10	Acetic acid	2.7	73

Decomposition of the Ethane in Acetic Acid.—The same procedure was followed here as in the decomposition of *sym.-p,p'*-tetramethyldiaminohexaphenylethane.

Ethane	Time, minutes	Absorption in cc. (22.5°, 761 mm.)	Per cent. absorption
0.10	3	2.2	60
.10	10	2.7	73
.30	45	2.0	18

A sample of the same ethane absorbed no oxygen whatsoever after ten minutes' solution in a mixture of equal parts of acetic acid and hydrochloric acid.

"Chichibabin Product" from Malachite Green.—Five **grams** of malachite green, dissolved in 100 cc. of concentrated hydrochloric acid, was reduced in an atmosphere of nitrogen with 25 cc. of 1 N chromous chloride. The reaction mixture was allowed to stand for five hours; it was then poured slowly, with constant stirring, into 1000 cc. of water in which 100 g. of sodium acetate was dissolved. The thick white amorphous precipitate which came out was filtered with suction, washed on the filter with water and dried in *vacuo.* The crude product weighed 3.7 g., 84% of the theoretical amount. It was crystallized from boiling n-butyl alcohol. The product weighed 2.6 g. and melted at 231–232°. Further crystallizations did not change this melting point.

The freshly prepared rearrangement product was a white crystalline solid, soluble without coloration in concentrated hydrochloric acid. On standing, the surface of the solid slowly turned green.

Anal. Calcd. for $C_{46}H_{50}N_4$: C, 83.8; H, 7.6. Found: C, 83.5; H, 7.4.

Molecular Weight, Micro Method.—Sample, 0.0150: camphor, 0.1353; average depression, 7.0". Calcd. for $C_{46}H_{50}N_4$: 658.6. Found: 634.

The Reaction of *Sym.-p,p',p'',p'''*-Octamethyltetraminohexaphenylethane with Sodium Amalgam.—Two grams of *sym.-p,p',p'',p'''*-octamethyltetraminohexaphenylethane was placed in a 100-cc. round-bottomed flask corked with a rubber stopper fitted with a straight glass stopcock. The flask was swept with nitrogen and partially evacuated; 40 cc. of anhydrous ether and 15 cc. of 1% sodium amalgam were then drawn into the flask. The flask was again swept with nitrogen, and was then shaken vigorously by hand. The color of the solution, originally light red, faded at once; in two minutes there was a momentary increase of color, which faded at once. A second similar run was made; when the transient color had reached its maximum, carbon dioxide was admitted to the flask. A small volume of gas was absorbed, but no acid could be isolated from the reaction mixture. Benzene was used as the solvent in a third similar run; the results were no more satisfactory. The ethereal solution of the decomposition products was separated from the excess amalgam, filtered and concentrated; the concentrate was diluted with ethyl alcohol. A gray-white crystalline product, melting at 93–95°, was isolated; a mixture of this product with *p,p'*-tetramethyldiaminotriphenylmethane[6] melted at 96–97". The product was apparently an impure sample of the leuco base of malachite green.

Long-Period Reduction of Malachite Green with Vanadous Chloride.—Two grams of malachite green and 2.0 g. of sodium acetate were dissolved in 20 cc. of acetic acid and 20 cc. of water. To this solution 10 cc. of 1 N vanadous chloride was added in the absence of air. The solution was allowed to stand for forty-eight hours; at the end of this time it was poured into 300 cc. of 5% sodium acetate solution. A copious light green precipitate appeared. The mixture was thoroughly extracted with chloroform; the united chloroform layers were washed, dried and concentrated. On dilution with ethyl alcohol, 1.1 g, of white crystals separated; after drying, the product melted at 93–94'. A mixture of these crystals and a known sample of *p,p'*-tetramethyldiaminotriphenylmethane melted at 95–96°.

The Reduction of Malachite Green with Titanous Chloride.—An experiment was carried out under conditions identical with those used in the preparation of *sym.-p-p',p'',p'''*-octamethyltetraminohexaphenylethane. One-half gram of malachite green was reduced with 15 cc. of 20% titanous chloride solution buffered with sodium acetate. The deep color of the malachite green disappeared at once. The solution was allowed to stand for three minutes, and was then diluted with 300 cc. of 5% sodium acetate solution. The precipitate of the free radical was filtered with suction. The filter paper and precipitate were placed in a bottle containing an upright test-tube filled with bromobenzene; this bottle was connected with an absorption buret. When equilibrium was established, the bromobenzene was allowed to flow onto the precipitate, and the absorption of gas was noted. The free radical representing 0.5 g. of the color salt absorbed 8.0 cc. at 21° and 752 mm.; this was 51% of the calculated absorption.

One-half gram of malachite green, dissolved in 45 cc. of water, was reduced in the absence of air with 10 cc. of 20% titanous chloride buffered with sodium acetate. The reduced solution was allowed to stand for forty-eight hours; it was then poured into an excess of alkaline sodium tartrate. The resulting suspension was thoroughly extracted with chloroform. The united chloroform layers were washed, dried and concentrated; on dilution with isopropyl alcohol 0.5 g. of a white crystalline solid came out. This was identified by a mixed melting point as *p,p'*-tetramethyldiaminotriphenylmethane.

Seven-tenths gram of malachite green was dissolved in 45 cc. of boiling water. To the boiling solution 10 cc. of 20% titanous chloride was added. Decolorization took place at once, and an amorphous sandy red precipitate appeared in the solution. The mixture was thoroughly extracted with chloroform; the united chloroform layers, washed and dried, were concentrated and diluted with isopropyl alchol. White crystals appeared in the solution; when isolated, they weighed 0.35 g., and melted at 93°. After one recrystallization their melting point was 95–96°. The product did not depress the melting point of a known sample of *p,p'*-tetramethyldiaminotriphenylmethane.

The Reaction of *Sym.-p,-p',-p'',-p'''*-Octamethyltetraminohexaphenylethane with Titanous Chloride.—A solution of 1.7 g. of *sym.-p,-p',-p'',-p'''*-octamethyltetraminohexaphenylethane and 5 g. of sodium acetate in 50 cc. of 80% acetic acid was treated in

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[6] Doebner, *Ann.*, 217, 255 (1883).

the absence of air with 10 cc. of 20% titanous chloride. The solution was allowed to stand for forty-eight hours; it was then diluted with sodium acetate solution and worked up in the usual manner. Five-tenths gram of *p,p'*-tetramethyldiaminotriphenylmethane was isolated; this represented 34% of the free radical. The remainder of the product was represented by a dark green tar from which no crystalline products could be isolated.

***p,p'*-Tetramethyldiaminotetraphenylethane.** (a) By Reduction of **Carbinol.**—One gram of p-dimethylaminodiphenylcarbinol was dissolved in 10 cc. of acetone; 5 cc of concentrated hydrochloric acid was added, followed by 10 cc. of 1 N chromous chloride. This mixture was allowed to stand in the absence of air for three hours. The reduction commenced at once, and the originally blue solution was deep green in fifteen minutes' time. When the reaction was complete, the reaction mixture was poured into 150 cc. of water; 20% aqueous sodium hydroxide was added until a precipitate of chromic hydroxide appeared. While still warm from the heat of neutralization, the mixture was thoroughly extracted with warm benzene. The united benzene extracts were washed with warm water, dried over sodium sulfate and concentrated by distillation to a volume of 8–10 cc. This solution was cooled and allowed to stand until crystallization of the high-melting isomer (m. p. 264–267°) was complete. The filtrate was concentrated to about 5 cc. and diluted with 10 cc. of boiling ethyl alcohol. On cooling, the low-melting isomer crystallized. The crude product was suspended in benzene at room temperature for five minutes; the suspension was filtered off and added to the major portion of the high-melting isomer. The low-melting isomer was brought out of the benzene solution by concentration and dilution with hot alcohol. After several such separations the product melted at 206–207°. The yields usually obtained were from 1 g.: 0.3–0.4 g. of low-melting isomer and about 0.2 g. of the other. The ratio of the two products was independent of the time of reduction. The reduction could also be carried out in glacial acetic acid 1.5 N in perchloric acid. The same procedure was followed as is outlined above; the two products appeared in the same ratio.

(b) By the Action of Sodium–Potassium Alloy upon *Sym.-p,p'*-**Tetramethyldiaminotetraphenylethylene.**—Three grams of *sym.-p,p'*-tetramethyldiaminotetraphenylethylene was suspended in a mixture of 15 cc. of anhydrous ether and 15 cc. of anhydrous benzene. This mixture was shaken in the absence of air for forty-eight hours with 3 cc. of sodium–potassium alloy. A greenish-blue color formed at once, which in the course of an hour's time gave place to a bright red coloration. The bright red potassium derivative was decomposed by the introduction of moist benzene. The contents of the flask were allowed to settle, and this crystalline residue was taken up with ordinary ether and treated with small amounts of ethyl alcohol until the alloy was decomposed. The benzene solution was washed thoroughly with water, dried over sodium sulfate and concentrated by distillation. Ethyl alcohol was added to the boiling concentrated solution; on cooling, 0.5 g. of a white crystalline solid came out. This, on recrystallization from benzene–alcohol, yielded 0.3 g. of a product which melted at 205–206°; a mixed melting point of this product and that prepared by reduction of *p*-dimethylaminodiphenylcarbinol with chromous chloride melted at 206–207°.

Anal. Calcd. for $C_{30}H_{32}N_2$: C, 85.7; H, 7.7. Found: C, 85.7; H, 7.7.

Molecular Weight, Cryoscopic, in Benzene.—Solvent, 9.91; samples, after preliminary seeding, 0.1403, 0.0965; depressions, 0.176°, 0.110°. Calcd. for $C_{30}H_{32}N_2$: 420. Found: 411, 426.

Analysis of High-Melting Isomer of *Sym.-p,p'*-Tetramethyldiaminotetraphenylethane.—(The melting point was 264–267°, with decomposition.) *Anal.* Calcd. for $C_{30}H_{32}N_2$: C, 85.7; H, 7.6. Found: C, 85.5; H, 7.6.

Molecular Weight, Cryoscopic, in Ethylene Dibromide.—Solvent, 23.54 g. sample, after preliminary seeding, 0.1518. A second sample did not wholly dissolve. Depression, 0.1795°. Calcd. for $C_{30}H_{32}N_2$: 420. Found: 424.

Molecular Weight, Micro Method.—Sample, 0.0139; camphor, 0.1020; depression, 13.9°. Found: 392.

Preparation of *p,p'*-**Tetramethyldiaminobenzophenone Dichloride.**—Five grams of Michler's ketone was dissolved in 150 cc. of anhydrous benzene. This solution was warmed to 30°; to the warm solution was added 3.5 g. of thionyl chloride. The solution turned an opaque blue and a dark oil separated at once. A slight evolution of sulfur dioxide was observed. The mixture was allowed to stand for a half-hour; during this time the oil crystallized on the bottom and sides of the flask. At the end of a half-hour the crystalline crust on the bottom of the flask was crushed with a stirring rod and the resultant suspension was filtered with suction. The crystalline cake was washed on the filter with benzene and then dried by a short exposure to the air. The yield was almost quantitative. The crude product was a bronze-green crystalline powder, the surface of which rapidly turned deep blue on exposure to the air. The product was used without further purification.

Reduction of the **Dichloride** in Acetone–Hydrochloric **Acid.**—*p,p'*-Tetramethyldiaminobenzophenone dichloride from 2.7 g. of Michler's ketone was dried for a short time, and then suspended in a mixture of 55 cc. of acetone and 5 cc. of concentrated hydrochloric acid. The deep blue solution thus formed was treated with 35 cc. of 1*N* **vanadous** chloride; the deep blue color of the dichloride disappeared at once. The reaction mixture was allowed to stand for two hours. At the end of this time the reaction mixture was diluted to 500 cc. with water, almost neutralized with aqueous sodium hydroxide, and thoroughly extracted with chloroform. The combined chloroform layers were washed with water, dried over sodium sulfate and concentrated. The boiling concentrated solution was diluted with boiling ethyl alcohol and again concentrated until crystals began to appear. The solution was cooled and filtered; the product weighed 1.25 g., representing 60% of the original ketone, and melted at 296°. The product did not depress the melting point of a known sample of *sym.-p*-octamethyltetramethyltetraminotetraphenylethylene prepared by the reduction of Michler's ketone with tin and hydrochloric acid.[7] The use of vanadous chloride and an acetic acid solution of the dichloride as well as chromous chloride in hydrochloric acid–acetone solution also yielded the ethylene.

Reduction of **Octamethyltetraminotetraphenylethylene** Glycol with **Chromous** Chloride.—One-half gram of the glycol was dissolved in 35 cc. of concentrated hydrochloric acid in a 50-cc. Erlenmeyer flask. Four cubic centimeters of *1 N* chromous chloride was added against a stream of carbon dioxide; the salt color disappeared immediately leaving a light green solution which grew deeper with the passage of time. The reaction was allowed to proceed for fourteen hours; then the reaction mixture was diluted. To the resulting solution was added 5.0 g. of sodium acetate; the solution was then almost neutralized with aqueous sodium hydroxide. A yellow amorphous precipitate came out of the solution during the neutralization. The mixture was extracted with chloroform; the united chloroform layers were washed with dilute sodium hydroxide, then with water and were dried over sodium sulfate. The dry filtered solution was concentrated and diluted with boiling ethyl alcohol; on cooling, 0.2 g. of *sym.-p,p'*-tetramethyldiaminotetraphenylethylene crystallized out of the solution. The product was identified by a mixed melting point. Another reduction was carried out under similar conditions, but was worked up after four hours' standing. Although the mother liquors were yellow, no crystalline ethylene could be isolated. A reduction using vanadous chloride was carried out under conditions identical with those described above,

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[7] Fischl, *Monatsh.,* 35, 525 (1914).

except that 5 cc. of 1 *N* vanadous chloride was used as the reducing agent. The product weighed 0.2 g.; it melted at 218–221°.

Reduction of *p*-**Dimethylaminophenylisopropylcarbinol.**—In a 25-cc. Erlenmeyer flask, 0.8 g. of *p*-dimethylaminophenylisopropylcarbinol[8] was dissolved in 15 cc. of concentrated hydrochloric acid. A vigorous stream of carbon dioxide was blown through the flask to sweep out the air; then 10 cc. of 0.75 *N* chromous chloride was added. The flask was again swept with carbon dioxide; it was then allowed to stand, tightly stoppered, for ten hours. The solution, originally blue, had a distinct greenish cast at the end of a half-hour; in about two hours, needle-shaped crystals of a double salt began to come out. When the reaction was complete, the crystals of the double salt were filtered off; these, after being washed with a little cold hydrochloric acid, were dried and reserved for the preparation of the high-melting isomer. The filtrate was diluted to four times its original volume, and was neutralized with dilute sodium hydroxide until a precipitate of chromic hydroxide appeared. While still warm from the neutralization, the mixture was extracted with warm benzene. The united benzene layers were washed with warm water, dried over sodium sulfate and concentrated. On cooling, a small amount of the high-melting isomer came out which was filtered from the mother liquors. The filtrate was heated to boiling and diluted with twice its volume of boiling ethyl alcohol. On cooling, 0.3 g. of the lower-melting isomer appeared in crystalline form. This product melted at 174°; further recrystallizations did not affect the melting point.

Anal. (low-melting isomer). Calcd. for $C_{24}H_{36}N_2$: C, 81.75; H, 10.3. Found: C, 81.35; H, 10.3.

Molecular Weight **Cryoscopic,** in Ethylene **Dibromide.**—Solvent, 19.75 g.; samples, after preliminary seeding, 0.1192, 0.1386. Depressions, 0.213°, 0.231°. Calcd. for $C_{24}H_{36}N_2$: 352. Found: 338, 350.

One-gram samples of p-dimethylaminophenylisopropylcarbinol were reduced with chromous chloride according to the method outlined above; for various times the yields were: after one hour, 20% low-melting isomer, no high-melting isomer; after four hours, equal amounts (20%) of both isomers; after twenty-four hours, 27% low melting, 38% high melting.

Preparation of High-Melting Isomer.—The double salt mentioned in the preparation of the low-melting isomer was dissolved in hot water, and the solution made strongly alkaline with ammonia. A voluminous white precipitate came out. The suspension was heated for an hour on a steam-bath, cooled and filtered with suction. After drying overnight *in vacuo* the crude product from 1.67 g. of double salt weighed 1.0 g. The product after crystallization from boiling benzene weighed 0.67 g. and melted at 239–240°.

Anal. Calcd. for $C_{24}H_{36}N_2$: C, 81.75; H, 10.3. Found: C, 80.7; H, 10.1.

Molecular Weight, Micro Method.—Sample, 0.0172; camphor, 0.1513; depression, 13.4°. Calcd. for $C_{24}H_{36}H_2$: 352. Found: 335.

Both isomers were unaffected by shaking with sodium–potassium alloy and by the action of concentrated hydrochloric acid.

Summary

1. The action of soluble reducing agents, such as vanadous chloride, on solutions of triphenylmethane dyes has been investigated using malachite green as an example, and *p*-dimethylaminotriphenylcarbinol as a transition compound between the dyes and triphenylcarbinol. The first

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[8] Sachs and Weigert, *Ber.*, 40, 4365 (1907).

product of the reaction is a free radical which may be isolated in the associated form (derivative of hexaphenylethane); it shows the typical behavior of these compounds. Under the influence of acids the free radical may further undergo rearrangement or reduction and oxidation to the corresponding methane and carbinol.

2. Michler's ketone dichloride and octamethyltetraminotetraphenylethylene glycol are both reduced by soluble reducing agents to octamethyltetraminotetraphenylethylene.

3. Dimethylaminodiphenylcarbinol and dimethylaminophenylisopropylcarbinol are each reduced by powerful soluble reducing agents with the formation of a pair of isomeric dimers.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTION OF ORGANIC HALIDES WITH PIPERIDINE. I. ALKYL BROMIDES

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RECEIVED NOVEMBER 15, 1930 PUBLISHED FEBRUARY 9, 1931

The reaction between a secondary amine and an organic halide is a common and useful method of preparation of tertiary amines. The reaction, as it is ordinarily carried out, is between two moles of the secondary amine and one mole of the halide with the formation of one mole of the tertiary amine and one mole of the secondary amine hydrohalide

$$2R_2NH + R'X \longrightarrow R_2NR' + R_2NH{\cdot}HX \qquad (1)$$

In a previous communication from this Laboratory[1] it was pointed out that certain halogen compounds did not follow the above reaction course with 3-methylpiperidine, but that the products obtained from the reaction were one mole of the secondary amine hydrohalide and one mole of unchanged secondary amine. No tertiary amine was isolated. Presumably, hydrogen halide had split out of the halogen compound with the formation of an unsaturated compound, thus

$$2R_2NH + R''X \longrightarrow R_2NH + R_2NH{\cdot}HX + (R''\text{—}H) \qquad (2)$$

There are scattered references[2] in the literature to the loss of a molecule of halogen acid from certain halides when they are treated with various organic bases, but apparently no effort has been made to study the reaction from this point of view.

It seemed desirable, therefore, to follow the rate and course of the reaction

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[1] Thayer and McElvain, THIS JOURNAL, 50, 3350 (1928).

[2] *Cf.* Houben–Weyl, "Die Methoden der organischen Chemie," Vol. IV, 1924, p. 243; Menschutkin, *Z. physik. Chem.*, 5,589 (1890); Wallach, *Ann.*, 230,233 (1885); Nef, *ibid.*, 309, 164 (1899).

between different types of organic halogen compounds and a representative secondary amine. Piperidine was chosen as the amine to be used on account of its availability in the pure state, high basicity and convenient boiling point. This paper reports the results obtained from the reaction of this secondary amine with eighteen alkyl bromides.

Each reaction was carried out in sealed tubes using two moles of piperidine and one mole of the alkyl bromide in petroleum ether as a solvent. The rate of reaction was followed by opening tubes from time to time and determining the amount of the insoluble piperidine hydrobromide which had precipitated. The course of the reaction was determined at the end of a suitable reaction period by precipitating and weighing the unreacted piperidine as piperidino-formanilide with phenyl isocyanate. The amount of tertiary amine which had formed could then be calculated as the difference between the amount of piperidine which had been put into the reaction and the piperidine which was recovered as the hydrobromide and as piperidino-formanilide. From these data the course of the reaction ((1) or (2) above) was apparent. The results which were obtained are tabulated in the experimental part of the paper.

Experimental

Materials Used

Piperidine.—Piperidine was prepared by the hydrolysis of benzoylpiperidine[3] with 10% sodium hydroxide solution. The piperidine was removed from this alkaline solution by distillation and converted to the hydrochloride by the addition of hydrochloric acid, The solution of the hydrochloride was then evaporated to dryness and the free base liberated from its salt with a saturated potassium hydroxide solution. The piperidine layer was separated, dried with solid potassium hydroxide and finally treated with metallic sodium and distilled. It boiled at 105.4–106".

The Alkyl Bromides.—Ethyl, n-propyl, isopropyl, *sec.*-butyl, *tert.*-butyl, diethylmethyl, *tert.*-amyl, benzyl and I-methylcyclohexyl bromides were prepared from the corresponding alcohols by the Norris procedure.[4] Isobutyl and isoamyl bromides were obtained by the action of phosphorus tribromide on the corresponding alcohols.6 *n*-Butyl, n-amyl, n-hexyl, n-heptyl, cyclohexyl, phenylethyl and phenylpropyl bromides were prepared by the method of Kamm and Marvel[6] from the corresponding alcohols. 1-Methylcyclohexyl bromide apparently has not been prepared before this time. It boiled at 65–66' (19 mm.); Br calcd., 45.1; found, 44.8; M_D calcd., 39.76; found, 39.86.

Phenyl isocyanate was purchased from the Eastman Kodak Company and was distilled before use.

The petroleum ether was washed with sulfuric acid and water. It was finally dried over sodium and distilled. It boiled at 50–75°.

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[3] Marvel and Lazier, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. IX, 1929, p. 16.

[4] Norris, Am. Chem. *J.*, 38, 641 (1907).

[5] Cf. Reynolds and Adkins, THIS JOURNAL, 51,279 (1929).

[6] Kamm and Marvel, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 1.

TABLE I

RATE OF THE REACTION BETWEEN PIPERIDINE AND VARIOUS ALKYL BROMIDES AT 90°

	% Reaction in									
Alkyl group	4	8	12	24	48	72	96	120	144	168 hr.
Ethyl	72.2	80.4	84.3	93.7	98.4	..	..	..	..	..
n-Propyl	45.6	59.5	66.2	79.3	89.5	..	..	..	..	..
Isopropyl	..	..	..	17.3	25.1	34.4	..	44.6	48.5	51.0
n-Butyl	46.1	59.3	66.5	78.0	88.4	..	..	..	..	..
Sec.-butyl	..	..	..	6.7	12.0	..	..	..	25.9	28.6
Isobutyl	10.0	16.0	..	29.4	40.8	..	..	57.0	..	..
Tert.-butyl	..	..	..	5.5	9.7	13.7	..	16.2	..	21.8
n-Amyl	48.1	63.6	69.8	80.7	90.5	..	..	..	..	..
Isoamyl	31.1	44.8	52.8	65.5	77.4	82.4	..	..	..	..
Diethylmethyl	..	..	..	6.2	9.9	13.1	..	18.3	..	23.6
Tert.-amyl	..	..	..	9.1	15.3	21.3	..	30.6	..	38.5
n-Hexyl	49.6	63.7	70.7	80.7	88.9	..	..	..	..	..
n-Heptyl	53.2	67.5	74.5	82.2	90.0	..	..	..	..	..
Cyclohexyl	..	..	..	1.1	2.4	..	3.3	..	..	6.5[a]
1-Methylcyclohexyl	..	..	..	7.2	12.5	17.4	21.9	25.7	..	..
Benzyl	100.5[b]	..	..	..	..	..	..	..	..	..
Phenylethyl	59.6	69.5	77.4	90.6	95.0	..	..	..	..	..
Phenylpropyl	74.0	83.9	86.4	93.2	95.8	..	..	..	..	..

[a] 11.2% in 384 hours. [b] 97.7% in 2 hours.

General Procedure

The determination of the rate of reaction between piperidine and each alkyl bromide was made in the following manner. In a test-tube prepared for sealing was placed 0.02 mole (1.700 g. delivered by a calibrated pipet) of piperidine and a solution of 0.01 mole (1.088–1.985 g.) of the alkyl bromide in 10 cc. of petroleum ether. This latter solution was a 10-cc. aliquot taken from a solution of 0.1 mole (10.88–19.85 g.) of the bromide in 100 cc. of petroleum ether. The tube was then sealed and placed in a thermostat held at 90°. Sufficient such tubes were prepared for each bromide to allow at least two tubes to be taken for the determination of each value given in Table I. When a tube was opened for a determination the precipitated piperidine hydrobromide was filtered off, washed with petroleum ether and dried. A portion of this precipitate was analyzed for its bromine content by titration with standard silver nitrate solution. These analyses showed in every case that the precipitate was practically pure piperidine hydrobromide. The remainder of the precipitate which adhered to the sides of the reaction tube and to the filter paper was washed into the solution resulting from the above titration and further titrated with the silver nitrate solution. From these determinations the amount of piperidine hydrobromide which had precipitated could be determined.

The results of these determinations are shown in Table I. Each value in this table is the average of at least two determinations. The calculation of the percentage reaction is based on the amount of alkyl bromide that was put into the reaction.

The determination of the course of the reaction was made after a sufficient time to allow for a reasonable amount of reaction, as shown by the above data on the rate of the reaction. The reaction tube was opened and the insoluble piperidine hydrobromide filtered off and washed with a few cc. of petroleum ether. The filtrate and washings were placed in a volumetric flask and made up to 50 cc. with petroleum ether. An aliquot, containing not more than 0.170 g.[7] of piperidine, of this solution was used for the determination of the unreacted piperidine. This aliquot was placed in a previously weighed weighing bottle (approximately 4 cm. in diameter and 6 cm. high) and made up to a volume of 30 cc. with petroleum ether. To this solution 1 cc. of phenyl isocyanate was added. A voluminous precipitate of piperidino-formanilide came down immediately. After standing for about ten minutes, the reaction mixture was filtered through a previously weighed Gooch crucible. The weighing bottle was rinsed with 10 cc. of petroleum ether and these rinsings used to wash the precipitate in the Gooch crucible. Since a small amount of the piperidino-formanilide always adhered to the side and bottom of the weighing bottle, it was dried along with the Gooch crucible in an oven at 80° and re-weighed. To the weight of piperidino-formanilide so obtained was added the weight (0.0024 g.) of the anilide which 40 cc. (the volume used in the determination) of petroleum ether was found to dissolve after several hours of shaking. By this procedure 98.5% of the piperidine was found in samples of petroleum ether containing 0.170 g. of the substance.

The results of such determinations for the eighteen alkyl bromides that were reacted with piperidine at 90° are shown in Table II. Each experimentally obtained value is the average of at least two determinations. All weights are expressed in moles X 10^2 in order to allow more ready comparisons and to avoid the use of a larger number of digits. Column B represents the moles of piperidine hydrobromide precipitated from the reaction and column C the moles of unreacted piperidine determined as piperidino-formanilide. Obviously the difference between the amount of piperidine (2 moles) originally put into the reaction and the piperidine recovered as the hydrobromide and as piperidino-formanilide would represent the amount of piperidine which had reacted to form tertiary amine. This value is shown in column D. Column E shows the amount of unsaturated compound formed and represents the difference between the amount of piperidine obtained as the hydrobromide (column B) and that amount of piperidine which was converted into the tertiary amine (column D).

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[7] Larger quantities of piperidine produced a too voluminous precipitate of piperidino-formanilide to be handled conveniently.

TABLE II

THE COURSE OF THE REACTION BETWEEN PIPERIDINE AND CERTAIN ALKYL BROMIDES AT 90°

Alkyl group	Reaction period, hours	A % reaction	B Moles × 10^2 piperidine hydrobromide	C Moles × 10^2 unreacted piperidine[a]	D Moles × 10^2 tertiary amine, 2-(B + C)	E Moles × 10^2 unsat. cpd. B − D
Ethyl	48	98.4	0.984	0.035	0.981	+0.003
n-Propyl	48	89.5	.895	.213	.891	+ .004
Isopropyl	168	51.0	.510	.994	.496	+ .014
n-Butyl	48	88.4	.884	.207	.909	− .025
Sec.-butyl	168	28.6	.286	1.390	.320	− .034
Isobutyl	120	57.0	.570	0.826	.604	− .034
Tert.-butyl	168	21.8	.218	1.781	.022	+ .196
n-Amyl	48	90.5	.905	0.183	.912	− .007
Isoamyl	72	82.4	.824	.335	.841	− .017
Diethylmethyl	168	23.6	.236	1.501	.263	− .027
Tert.-amyl	168	38.5	.385	1.517	.097	+ .288
n-Hexyl	48	88.9	.889	0.222	.889	.000
n-Heptyl	48	90.0	.900	.196	.904	− .004
Cyclohexyl	384	11.2	.112	1.766	.121	− .009
1-Methylcyclohexyl	120	25.7	.257	1.629	.113	+ .114
Benzyl	4	100.5	1.005	0.003	.992	+ .013
Phenylethyl	48	95.0	0.950	.047	1.003	− .053
Phenylpropyl	48	95.8	.958	.044	0.998	− .040

[a] Determined as piperidino-formanilide.

It is seen from Table II that certain secondary and tertiary bromides did not show sufficient reaction at 90° to permit the determination of the course of the reaction to have much meaning. For this reason it seemed desirable to repeat the experiments with these bromides at a higher temperature in the hope of bringing about more complete reaction. This was done by heating the reaction tubes in an oil-bath kept at 125–135° by a hot-plate. No attempt was made to control the temperature as accurately as in the experiments summarized in Table II. After the indicated reaction period the tubes were cooled, opened and the reaction product determined

TABLE III

THE COURSE OF THE REACTION BETWEEN PIPERIDINE AND CERTAIN SECONDARY AND TERTIARY ALKYL BROMIDES AT 125–135°

Alkyl group	Reaction period, hours	A % reaction	B Moles × 10^2 piperidine hydrobromide	C Moles × 10^2 unreacted piperidine[a]	D Moles × 10^2 tertiary amine 2-(B + C)	E Moles × 10^2 unsat. cpd., B − D
Isopropyl	48	73.7	0.737	0.456	0.807	−0.070
Sec.-butyl	24	43.5	.435	1.122	.442	− .007
Tert.-butyl	24	47.2	.472	1.400	.128	+ .334
Tert.-amyl	72	99.1	.991	0.926	.083	+ .908
Cyclohexyl	120	81.1	.811	1.068	.120	+ .691
1-Methylcyclohexyl	120	89.5	.895	0.981	.124	+ .771

[a] Determined as piperidino-formanilide.

in the same manner as that described above for the experiments run at 90°. The data for these experiments are summarized in Table III. Each experimentally obtained value in this table is the average of at least two determinations.

Discussion of Experimental Results

It is seen from Table I that there is an enormous difference in the reactivities of the three types of alkyl bromides with piperidine. As a class the primary bromides react quite completely in forty-eight hours. An exception is noted in the case of isobutyl bromide and this is due, no doubt, to the proximity of the branching in the chain to the halogen atom, for isoamyl bromide shows a distinctly greater reactivity than isobutyl bromide. Further, it may be pointed out that there appears to be a distinct alternating effect of the phenyl group on the reactivity of benzyl, phenylethyl and phenylpropyl bromides when they are compared after a four-hour period of reaction. The secondary and tertiary bromides are exceedingly unreactive when compared to the primary bromides. This fact is strikingly shown by the percentage of reaction in the forty-eight hour column of Table I. In this unreactive group cyclohexyl bromide is by far the least reactive. Conant and Hussey[8] have previously noted the extraordinary inertness of cyclohexyl chloride in their study of the rate of reaction of various alkyl chlorides with potassium iodide in acetone solution. They attributed this abnormal behavior to the cyclohexane ring. It is quite possible, however, that the reactivity which the other secondary bromides show may be due to a previous rearrangement to the more reactive primary bromide and that the unreactivity of the cyclohexyl bromide is due to the fact that it cannot rearrange to such a form.

The data summarized in Table II indicate that the primary and secondary bromides react to form tertiary amines, while the three tertiary bromides show a decided tendency to lose hydrobromic acid to form, presumably, an unsaturated compound. A relatively small positive value in column E carries no significance and, traced back to its source, probably means that the value obtained for the moles of unreacted piperidine (column C) rather than the corresponding value in column B was too high. A negative value in column E indicates that the amount of tertiary amine formed (column D) is greater than the amount of piperidine precipitated as the hydrobromide (column B). Obviously, such a ratio of reaction products is theoretically impossible, and when it is indicated it is due to a too low value in column B or C. As a group, however, the primary and secondary bromides in Table II show that there is formed practically the same number of moles of tertiary amine as of piperidine hydrobromide. The tertiary bromides, on the other hand, show a marked difference between the moles of tertiary amine and piperidine hydrobromide produced.

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[8] Conant and **Hussey, THIS JOURNAL, 47,479** (1925).

The amount of reaction which most of the secondary and tertiary bromides in Table II show is relatively small. **Table** III gives a better view of the behavior of these compounds. At this higher reaction temperature it is seen that isopropyl and secondary butyl bromide definitely react to form a tertiary amine, but that cyclohexyl bromide, which appeared to be showing the same type of reaction in Table II, when forced into a more complete reaction shows practically the same tendency as the tertiary bromides to lose hydrobromic acid and forms only a relatively small amount of a tertiary amine. This fact would seem to lend further support to the suggestion made above that the secondary bromides which react with piperidine to form a tertiary amine probably rearrange to primary bromides before reacting and react as such. This possibility will be tested experimentally in this Laboratory and the results reported later. The tertiary bromides in Table III follow more completely the course which they started in Table II.

Summary

1. The rate and course of the reaction between piperidine and eighteen alkyl bromides has been determined.

2. It has been found that the primary and secondary bromides, with the exception of cyclohexyl bromide, react with piperidine to form tertiary amines. Cyclohexyl bromide and the tertiary bromides which were studied react, in the main, to lose hydrobromic acid and form, presumably, an unsaturated compound.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO]

STUDIES IN PROTEINS.
II. CONCERNING THE UNIFORMITY OF THE PROTEIN FRACTION EXTRACTED FROM ORANGE SEED MEAL BY SALT SOLUTIONS

BY FELIX SAUNDERS

RECEIVED NOVEMBER 15, 1930 PUBLISHED FEBRUARY 9, 1931

Introduction

In a series of recent papers, Gortner and his co-workers[1] have reported the results of studies on the "peptization" of wheat flour proteins. Their figures show a great variation in the fraction of the total nitrogen extracted by various salts. From their data, the authors draw the following conclusions: (1) both anions and cations show a lyotropic series, (2) "protein 'solubility' in neutral salt solutions is, in reality, protein peptization, and

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[1] Gortner, Hoffman and Sinclair, Cereal Chemistry. 6, 1 (1928); "Colloid Symposium Monograph," The Chemical Catalog Co., Inc., New York, 1928, Vol. V, p 179.

as such it is governed as to rate and extent by the nature of the particular anions or cations present in the salt solution," (3) "we do not believe that any salt used, in any one of the concentrations, extracts a chemical entity which should be designated by the term 'globulin'."[2] While Gortner's conclusions seem entirely justified with respect to the systems with which he worked, they do not seem to apply in the case of a system containing a representative crystalline globulin. In the present paper, studies are reported similar to Gortner's except that they were made on material in which most or all of the nitrogenous substance was crystalline globulin. Furthermore, a crystalline globulin was isolated using the different salts as extracting agents and the percentage of nitrogen in the protein determined in each case.

Material.—The material used in this study was orange seeds,[3] which yield a crystalline globulin, pomelin.[4] The whole seeds were ground in a Wiley mill. The oil was removed by repeated extractions with benzol. The meal which was left after filtering off the benzol was air-dried and then sifted. The fraction which passed through the 40-mesh sieve but not through the 60-mesh was used.

Method.—In order to have the results comparable, Gortner's procedure was followed as closely as possible in the extraction studies. Six grams of the orange seed meal was placed in a centrifuge bottle and covered with 50 cc. of the solution of the salt being investigated. The suspension was shaken mechanically for thirty minutes, centrifuged, and the supernatant liquid was poured into a Kjeldahl flask. Two more extractions were carried out in the same way. The nitrogen in the combined extractions was determined by the usual Kjeldahl procedure.

The pure protein was isolated in the following way. One liter of the salt solution was warmed to 55° and added to 100 g. of the seed meal. The mixture was allowed to stand for about two hours without any further warming. After as much of the liquid as possible had been recovered by centrifuging, solid ammonium sulfate was added to saturation. The globulin which precipitated was separated in the centrifuge and then redissolved by adding distilled water. Any undissolved material was removed by centrifuging and the solution was dialyzed in viscose bags[6] against cold, running, distilled water for about sixty-four hours. The supernatant liquid was separated from the protein precipitate by centrifuging. With-

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[2] These statements were intended to apply only to wheat flour.

[3] These seeds were supplied by the California Fruit Growers Exchange. It is a pleasure to be able to acknowledge their courtesy in collecting and sending this material.

[4] Pomelin is the name which has been given to the crystalline globulin isolated from citrus seeds. It is easily obtained as octahedral crystals by the dialysis of a salt solution of the protein. A more detailed report on this protein will be published soon.

[5] Grateful acknowledgment is made to the Visking Corporation for furnishing the viscose tubing used in this work.

out being removed from the centrifuge cup, the protein was washed by suspending it in successive portions of alcohol of gradually increasing concentration starting with 40% and running up to absolute. The protein was then filtered off and washed with absolute ether. Finally it was dried to constant weight in a vacuum oven at 50°. The protein prepared in this way is a snow-white powder which easily passes through a 100-mesh sieve without any grinding. Each preparation of protein was examined under the microscope during dialysis to be sure that crystallization was proceeding properly.

As a further check, the residue from the protein extraction was dried on the steam-bath, ground until it all passed through a 60-mesh sieve and then analyzed for nitrogen. Of course, a correction for residual salt had to be made. At first an attempt was made to determine salt directly by ashing but this method proved unsatisfactory. An indirect calculation of the salt content on the basis of the amount of liquid left in the meal after centrifuging was much more trustworthy.

Experimental.—The experimental data are summarized in the following table. The variation in the yield of globulin can be explained by technical difficulties. In the case of the sodium bromide and potassium bromide some of the material was accidentally lost. The discrepancy in the values of the nitrogen in the residue from the extraction with sodium iodide and potassium iodide has been accounted for by difficulties in ash determination.

TABLE I

SOLUTION OF THE PROTEIN OF ORANGE SEED BY NORMAL HALIDES

Salt	% of total N extracted	Grams of N in 100 g. of residue	Yield of globulin, grams	N in protein, %
LiCl	72.5	3.1	7.02	16.9
NaCl	72.5	3.0	5.36	17.1
KCl	73.4	3.0	5.62	17.1
LiBr	73.9	3.0	6.80	16.9
NaBr	73.4	2.8	3.42	16.8
KBr	74.2	2.8	3.56	17.0
NaI	73.9	2.4	5.52	16.8
KI	73.4	3.4	6.90	17.0
Average	73.4	2.9	5.53	16.9

Discussion

The experimental data show very clearly that the alkali halides are alike in their ability to extract the protein of orange seeds. This finding is confirmed by the analysis of the residue. Considered by themselves, the analytical figures would not prove that the protein isolated was always the same. However, when taken in conjunction with the extraction figures, they probably warrant the conclusion that the protein is the same in every case. Furthermore, the crystal form and general behavior were the same in every preparation.

According to Gortner, a normal solution of potassium chloride extracts from wheat flour 23% of the total nitrogen, potassium bromide extracts 37% and potassium iodide extracts 64%. Using the same technique on orange seed meal, the figures obtained were: potassium chloride, 73.4; potassium bromide, 74.2; and potassium iodide, 73.4. The difference between the figures of the two series is of no significance since they were obtained on different materials, but the variation between results within each series is important. The first set shows a definite lyotropic series but the variation within the second series is no greater than the experimental error.

The discrepancy may be the result of differences in the type of materials used. Wheat flour contains a complex mixture of proteins in which gliadin and glutenin predominate. It is, therefore, hardly a suitable substance for the study of the action of salt solutions on globulins, even if we assume that flour contains a globulin fraction. Gortner's results justify the statement that all the material extracted by salt solutions from wheat flour is not necessarily globulin, but they do not force the conclusion that there is no such thing as a chemical entity which we may designate "globulin." In fact, of all the proteins there are probably none better entitled to consideration as chemical entities than the crystalline globulins. The real need is a definition which will distinguish between the crystalline or semicrystalline globulins and the nitrogenous material which can be extracted from almost any biological material.

In a private communication, Dr. Gortner asserts that he had no intention of denying the existence of globulins but was merely questioning the definition of the globulins and the methods for isolating them. Unfortunately many persons have construed his remarks to mean a complete denial of the existence of globulins as a class of proteins. It should be noted that Gortner's statements were made only in connection with the wheat flour system which he studied and it is not intended in this paper to imply that he wished at any time to extend his conclusions to other systems.

The question remains whether the existence of a lyotropic series in the extracting power of various salts may not still be demonstrated even in representative seed materials which are known to yield crystalline globulins. Dr. Gortner has very kindly sent the author a private communication in which he gives some figures from recent work in his laboratory. His results show very conclusively that there may be a series even with seeds which give a crystalline globulin. However, the existence or nonexistence of such a lyotropic series need not affect the other considerations regarding the nature of the protein extracted. In other words, different salt solutions may show a variation in their peptizing power toward a given system and yet be extracting the same protein only in varying amounts.

Unpublished results from this Laboratory show that the foregoing statement is probably true in some cases at least. Of course, the converse may also be true, that is, different salts may extract the same amount of nitrogen from a meal and yet may not be extracting a chemical entity.

This study is being extended to include other seeds known to yield crystalline globulins, and different salts at varying concentrations are also being used.

Conclusions

1. The alkali halide salts in normal concentration all extract the same amount of nitrogen from orange seed meal. There is no evidence for the existence of a lyotropic series in the extracting power of different salts on orange seed meal.
2. The protein isolated from orange seed meal by extraction with different salts is probably the same in every case.

CHICAGO, ILLINOIS

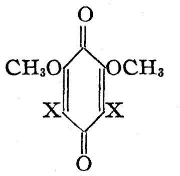
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

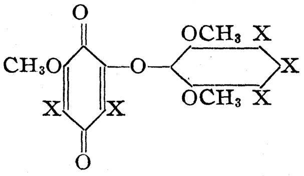
A NEW TYPE OF OXIDATION PRODUCT DERIVED FROM QUINONES[1]

BY W. H. HUNTER AND MURRAY M. SPRUNG

RECEIVED NOVEMBER 17, 1930 PUBLISHED FEBRUARY 9, 1931

During a study of the oxidation of tribromo- and trichloropyrogallol-2,6-dimethyl ether, Hunter and Levine[2] showed that when treated with any of a number of oxidants, these phenols gave both a yellow mononuclear quinone (I) and a red (or purple) phenoxy quinone (II).





I (X = Br or Cl) II

However, when the oxidations were carried out with chromium trioxide in 50% acetic acid[3] there were obtained, in addition to these expected products, small amounts of colorless compounds. These compounds seemed to be of a nature different from any of the oxidation products previously isolated during this series of investigations. Their further study therefore

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[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1928.

[2] Hunter and Levine, THIS JOURNAL, 48, 1608 (1926); cf. Hunter and Morse, *ibid.*, 48, 1615 (1926).

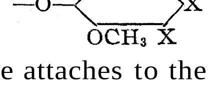
[3] Hunter and Levine, Ref. 2, p. 1612.

appeared to be of interest, and was undertaken, leading to the results described in the present paper.

A quantity of each of the colorless oxidation products was prepared and very carefully purified. On subjecting them to ultimate analyses and molecular weight determinations, a pair of empirical formulas was obtained which at first sight do not seem to be related. For the colorless oxidation product of tribromopyrogallol-2,6-dimethyl ether the best formula is $C_{28}H_{22}O_{15}Br_8$ (calculated molecular weight, 1238); for the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether the best formula is $C_{14}H_{11}O_8Cl_4$ (calculated molecular weight, 449). Nor do these formulas have any apparent relation to either of the normal products of oxidation of the phenols, for the mononuclear quinones have the composition, $C_8H_6O_4Br_2(Cl_2)$, while the dinuclear quinones have the composition, $C_{15}H_9O_6Br_5(Cl_5)$. Furthermore, the colorless substances are much richer in oxygen than any of the expected products. We were therefore led to suspect that oxidative rupture had occurred at some stage of these oxidations.

It was later discovered that the colorless compounds could also be obtained directly from the corresponding dinuclear quinones (II) of Hunter and Levine, by oxidizing the latter with chromium trioxide under conditions identical with those used in the synthesis of the colorless compounds from the trihalogenated pyrogallol-dimethyl ethers, showing that the colorless compounds are probably secondary products, derived from oxidation of the primary quinones.

A second very significant reaction was found to occur when dilute alkali was added to the colorless substances. Both compounds went into solution quite rapidly. On acidification of the solution, immediate precipitates of colorless materials were produced which were, *in both cases, different from the starting materials.* Investigation proved them to be the *original trihalogenated pyrogallol-dimethyl ethers* from which the colorless oxidation products, themselves, are derived. This action was very rapid, and in the case of the brominated compound it was demonstrated that the yield of phenol obtained was constant, that is, 63.2% of the weight of the brominated oxidation product used. It is therefore evident that the white compounds contain the residue

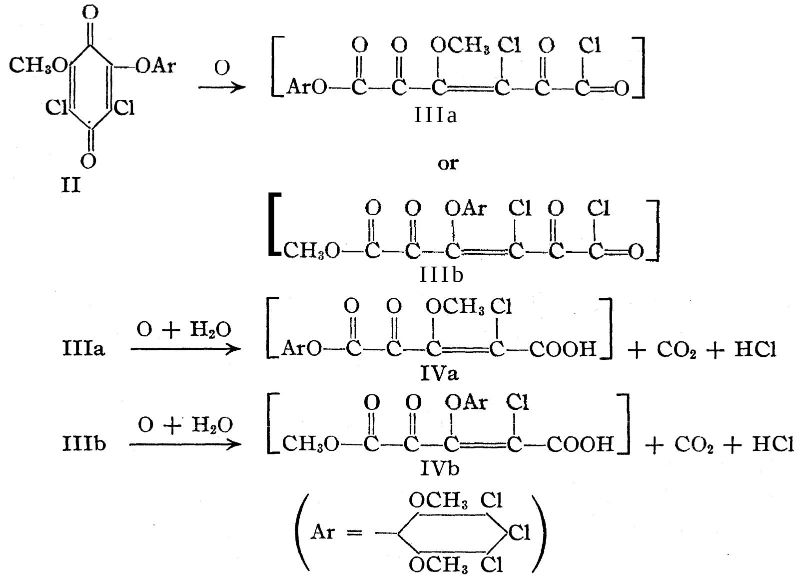


(X = Br or Cl)

and that this residue attaches to the rest of the molecule by some easily saponifiable linkage, for which only two simple possibilities suggest themselves: an ester linkage, and an acetal or hemiacetal linkage.

If now we consider the chlorinated oxidation product first (because of its simpler analytical formula, $C_{14}H_{11}O_8Cl_4$) we may arrive at a theory for its formation on the basis of the above information only. Three significant facts must be accounted for at this time: first, one carbon atom is lost when the white compound is produced from the phenoxy quinone; second, the colorless compound still contains the phenoxy group as a distinct unit, easily lost by saponification; third, when the phenoxy residue is removed from the colorless compound, the resulting residue is easily and apparently completely destroyed by the reagent.[4]

A series of steps leading from the purple dinuclear quinone (II) to a product (IV) of the desired empirical'composition is outlined below.



On the basis of the well-known oxidation of quinone to maleic acid,[5] it might reasonably be expected that if the chlorinated phenoxy quinone (II) were subjected to the action of a sufficiently strong oxidant, the first effect would be to split the quinonoid ring open at one of the double bonds. One oxygen atom would add to each side of the ruptured bond, and there would result one of two compounds, IIIa or IIIb, depending upon which double bond of the quinone ring was ruptured. Either of the hypothetical compounds thus produced is a di-acid derivative: the first a substituted phenyl ester and an acid chloride; the second a methyl ester and an acid chloride. It is important, also, that each is **twice** an *alpha oxo acid* derivative, that is, an alpha oxo acid chloride and an alpha oxo ester. Now alpha oxo esters are quite stable toward oxidation (pyruvic ester, for example). However, we have been able to find no mention in the literature

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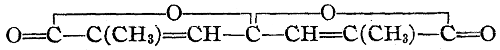
[4] Many attempts were made to isolate this residue after the "hydrolytic" reaction, but in no case could a single, homogeneous product be obtained In all such cases, large amounts of halogen acid and some oxalic acid were found in the solution.

[5] **Kempf,** ***Ber.*,** **39,** 3719 (1906).

of the existence of alpha oxo acid chlorides. We consider it quite probable that such a compound, under the conditions of our experiments, would either be hydrolyzed to the free alpha oxo acid and then further oxidized, or oxidized directly as the oxo chloride. In either case, we should expect to find the carbon chain lessened by one carbon atom, to give a C_{14} compound. There would result, then, a complicated alpha oxo ester of an unsaturated 5 carbon di-acid (IVa or IVb).

The formulas IVa and IVb are of course isomeric, and correspond empirically to the composition $C_{14}H_{10}O_8Cl_4$. The experimental formula for the chlorinated colorless oxidation product is $C_{14}H_{11}O_8Cl_4$, identical with the above except for one hydrogen, a discrepancy which could easily be accounted for by a relatively slight error in hydrogen analysis.

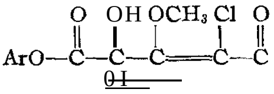
However, our colorless compound has no effect upon saturated sodium hydrogen sulfide, and it, therefore, cannot be a carboxylic acid. Furthermore, it forms a well-defined acetyl derivative, which can be crystallized unchanged from ethyl alcohol, and is, therefore, not a mixed anhydride. We conclude from this that our acid, which would be a gamma oxo acid, exists in the oxy-lactone form, similar to the alternate formula for levulinic acid, $CH_3\underbrace{C(OH)CH_2CH_2C}_{O}{=}O$. Levulinic acid, too, is known to form an acetyl derivative, which also can be crystallized unchanged from ethyl alcohol, and to which the formula $CH_3\underbrace{C(OCOCH_3)CH_2CH_2C}_{O}{=}O$ has been assigned.[6] Unsaturated gamma oxo acids show the same tendency toward lactone formation. Thus acetone dipyruvic acid exists only in the form of a dianhydro compound to which the formula



$$O{=}\overbrace{C{-}C(CH_3){=}CH{-}C}^{O}\overbrace{{-}CH{=}C(CH_3){-}C}^{O}{=}O$$

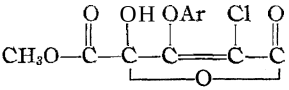
has been assigned.

If our white oxidation product is a gamma oxy lactone, it may have either of the following formulas



$$ArO{-}\overset{O}{\overset{\|}{C}}{-}\underbrace{\overset{OH}{\overset{|}{C}}{-}\overset{OCH_3}{\overset{|}{C}}{=}\overset{Cl}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}}_{O}$$

Va



$$CH_3O{-}\overset{O}{\overset{\|}{C}}{-}\underbrace{\overset{OH}{\overset{|}{C}}{-}\overset{OAr}{\overset{|}{C}}{=}\overset{Cl}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}}_{O}$$

Vb

To choose between these two formulas, it need only be remembered that the substituted phenoxy group is easily saponified, the methoxy group not. Therefore the substituted phenyl group must be tied by an ester linkage, and the methyl group by an ether linkage. All this evidence points to formula Va as representing the most probable structure for the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether. Its acetyl derivative would then have the structure

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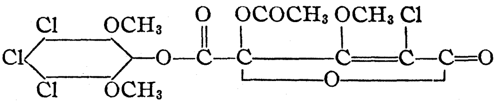
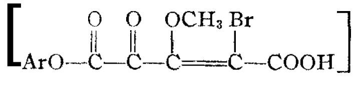
[6] Bredt, *Ann.*, 236, 225 (1886); *ibid.*, 256, 314 (1890); Autenrieth, *Ber.*, 20, 3191 (1857); Thiele, Tischbein and Lussow, *Ann.*, 319, 184 (1901).



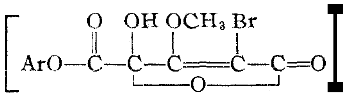
The colorless brominated oxidation product is similar to the chlorinated compound both as regards mode of formation and chemical behavior. The two compounds behave analogously in respect to a variety of chemical reagents. However, a series of carefully checked analytical data and molecular weight determinations has established the previously mentioned C_{28} formula, *i.* e., $C_{28}H_{22}O_{15}Br_8$. Assuming the hydrogen analyses to be high again, we may modify this formula (for reasons which will shortly be clear) to $C_{28}H_{18}O_{15}Br_8$. If the brominated compound were exactly analogous to the chlorinated compound it would have the composition $C_{14}H_{10}O_8Br_4$. It is then evident that the formula $C_{28}H_{18}O_{15}Br_8$ represents a *dimolecular* anhydride of the simpler formula $C_{14}H_{10}O_8Br_4$.

The most reasonable mechanism by which to explain the formation of the brominated oxidation product is as follows: as in the case of the analogous chlorine compound, a monomolecular derivative is first formed. This may possess either the free acid structure (VIa), or the gamma oxy-lactone form (VIb).

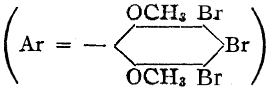


$$\left[ArO{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{OCH_3}{\overset{|}{C}}{=}\overset{Br}{\overset{|}{C}}{-}COOH\right]$$

VIa



VIb



But, as we have previously mentioned, there is a definite tendency for the hydroxyl group of a gamma oxy lactone to become esterified through dilactone formation. When this is impossible, dehydration sometimes occurs, by loss of the hydroxyl group along with an alpha hydrogen atom. The above hypothetical gamma oxo acid, however, has neither a second gamma carboxyl group nor an alpha hydrogen atom. The tendency toward reaction can only be satisfied, in this case, by elimination of water between two molecules and this leads to the dimolecular anhydride which is actually isolated.[8]

There are at least three possible mechanisms by which the formation of a dimolecular anhydride may be explained, assuming that such anhydride formation actually does occur. There may be formed in the solution both

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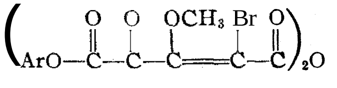
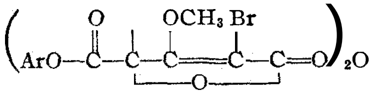
[7] Stating this in another way, the only "available" hydrogen atom which can split out with the hydroxyl group of one molecule is the hydroxyl hydrogen of a second molecule.

[8] The chloro and the bromo hypothetical intermediates, then, behave differently under the same experimental conditions. It is not entirely clear just why they should do so; but there is, on the other hand, no a *priori* reason to assume that they must behave the same.

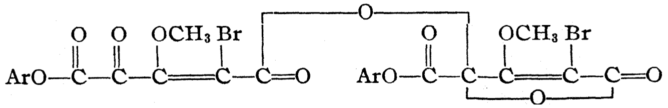
the free acid form and the lactone form (formulas VIa and VIb). The free acid, instead of becoming esterified intramolecularly, as in the case of the analogous chloro compound, may become esterified intermolecularly, and this may occur either by union with a second molecule of the free acid itself, or by union with a molecule in the oxy lactone form. In the first case, the ordinary type of acid anhydride (formula VIIa) would result; in the second case, the product would be an unsymmetrical molecule (formula VIIb).



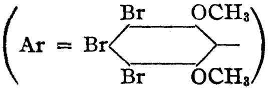
VIIa



VIIc

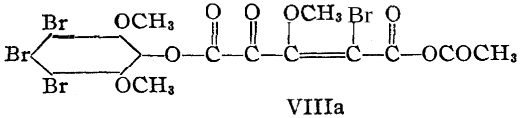


VIIb

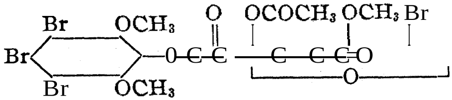


The third possibility is that only the lactone form of the acid (VIb) is involved in intermolecular anhydride formation. The dimolccular anhydride would then have the structure VIIc. It is possible to eliminate the first of these structures (formula VIIa) by virtue of the fact that the compound can be crystallized unchanged from ethyl alcohol, and therefore cannot be a normal acid anhydride. It is impossible at present to make a choice between formulas VIIb and VIIc.

The colorless oxidation product of tribromopyrogallol-dimethyl ether, like the analogous chloro compound, forms an acetyl derivative, when subjected to the action either of acetic anhydride and glacial acetic acid, or acetyl chloride and concentrated sulfuric acid.[9] This acetyl derivative has the composition $C_{16}H_{12}O_9Br_4$, and is therefore derived from the monomeric form of the acid. Its structure may be either that of a mixed anhydride VIIIa or an acetylated gamma oxy lactone VIIIb, again.



VIIIa



VIIIb

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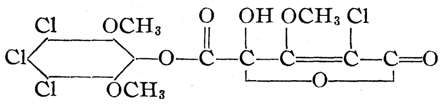
[9] The hydrogen necessary for this reaction may come from the sulfuric acid used during the acetylation. Very little water is required, due to the very large molecular weight of the colorless oxidation product.

We are once more inclined to favor the gamma oxy-lactone formula (VIIIb), by analogy with the acetyl derivative of levulinic acid and of our chlorinated oxidation product. Moreover, this acetyl derivative also may be crystallized unchanged from alcohol, which is evidence against the mixed anhydride formula. Further evidence for structure VIIIb is that whereas the acetyl derivative is broken down to the original phenol by dilute alkali, as is the white compound itself, in the former case the hydrolysis requires boiling alkali, while the unacetylated derivative breaks down quite easily in the cold. In formula VIIIb the oxo group alpha to the substituted ester grouping is modified in such a way as would be expected to stabilize the ester group toward hydrolysis, while in formula VIIIa no such modification is suggested.

Conclusions

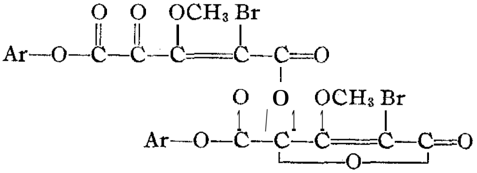
1. From these considerations we suggest IX as the most probable formula for the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether



IX

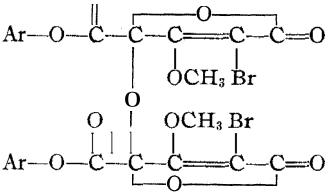
the oxy-lactone of α-chloro-β-methoxyquinonic[10] acid [(3,4,5-trichloro-2,6-dimethoxy)-phenyl ester].

2. Either Xa or Xb then becomes the best formula for the colorless oxidation product of tribromopyrogallol-2,6-dimethyl ether.



Xa

Ester of IX (bromine analog)
keto form



Xb

Ether of IX (bromine analog)
Ar = $—C_6Br_3(OCH_3)_2$

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[10] In order to simplify the naming of these structures, it is convenient to designate the parent acid (a-keto-glutaconic acid, COOHCOCH═CHCOOH) by some suitable trivial name. We have adopted the name "quinonic acid," since a like oxidation of parabenzoquinone would yield this acid, if it could be carried out.

At the present time we wish to present these formulas provisionally only. Although these structures are as yet by no means rigorously established, we nevertheless consider them to be entirely plausible, in so far as they agree with *every one* of the known experimental facts and satisfy the analytical requirements admirably. We hope to be able to test these suggested structures by further chemical investigation of the substances and of analogous materials.

Experimental Part

Oxidation of Tribromopyrogallol-2,6-dimethyl Ether.—A representative procedure was as follows. Nine grams of tribromopyrogallol-2,6-dimethyl ether (m. p. 134.2°) was covered with 900 cc. of 50% acetic acid and warmed on a water-bath to 80°, at which temperature the dimethyl ether went into solution. Six and six-tenths grams (3 molar equivalents) of chromium trioxide was stirred in. An immediate precipitate of the purple phenoxy quinone was usually obtained. This varied somewhat in quantity, and in one or two cases no phenoxyquinone was formed. The temperature was maintained at 80° for fifteen to twenty minutes, after which the mixture was cooled, and filtered from the phenoxyquinone. It was then poured, slowly and with stirring, into 1200 cc. of cold water, and allowed to stand. The white oxidation product appeared as a very flocculent precipitate, which slowly settled to the bottom of the vessel. After several hours, most of the supernatant liquid was decanted, and the white compound filtered onto a good grade of coarse filter paper made into a "fluted filter." It was washed with dilute acetic acid, water and dilute (ca. 25%) alcohol and allowed to dry between filter papers. Eight oxidations, each starting with 9 *g.* of the phenol, gave an average of 2.9 g. of the colorless compound, or about 32% of the weight of the starting material. The yield was greatly reduced when the oxidation was carried out with larger amounts of the phenol.

The colorless compound melted, when crude, at 193–197°. A sample was purified by recrystalliiation, as follows: four times from dilute ethyl alcohol, once from aqueous ethyl acetate, three times from dilute methyl alcohol, twice from aqueous methyl acetate and finally once again from dilute methyl alcohol. Starting now with a bath temperature of 200°, the substance showed a melting point of 206–206.6" (with decomposition). A sample obtained from the last methyl alcohol–water filtrate by evaporating to dryness melted with decomposition at 206–207° (Jackson's test for purity).

Anal. Subs., 0.1842, 0.1977: AgBr (Carius), 0.2258, 0.2413. Subs., 0.1955, 0.2022: CO_2, 0.1940, 0.2006: H_2O, 0.0318, 0.0325. Subs., 0.1747, 0.1709: AgI (Zeisel), 0.1936, 0.1922. Calcd. for $C_{28}H_{18}O_{15}Br_8(6\ OCH_3)$: C, 27.23; H, 1.46; Br, 51.86; O, 19.45; OCH_3, 15.08; $C_8H_6O_3Br_3$ (hydrolyzable), 63.2; mol. wt., 1234. Found: C, 27.06, 27.04; H, 1.81, 1.80; Br, 52.17, 52.04; O (by difference), 19.96, 20.12; OCH_3, 14.64, 14.86; $C_8H_6O_3Br_3$ (hydrolyzable), 63.2, 63.3; mol. wt. (in ethylene dibromide), 1241, 1208, 1215, 1110, 1150, 1260; mol. wt. (in camphor), 1226, 1515.

Properties of the Colorless Oxidation Product of Tribromopyrogallol-2,6-dimethyl Ether.—This substance crystallizes from dilute ethyl alcohol in pure white, microscopic needles, melting, when very pure, at 206–206.6° (decomp.). It is very soluble in acetone, acetic acid, ethyl acetate, methyl acetate and chloroform; moderately soluble in methyl alcohol, and ethyl alcohol; slightly soluble in amyl alcohol, toluene, benzene, xylene, ethylene dibromide, acetophenone and hot carbon tetrachloride; practically insoluble in cold carbon tetrachloride, water and ligroin.

It is oxidized only very slowly by hot alkaline permanganate, hot acid permanganate and boiling concentrated nitric acid. Boiling silver nitrate in 95% alcohol produces only a slight murkiness. It dissolves in concentrated sulfuric acid to a clear solution. Such a solution was diluted with water, leading to the precipitation of a white material, which was shown to he tribromopyrogallol-2,6-dimethyl ether (m. p. 131–136°).

The original oxidation product is entirely unaffected by any of the following reagents: boiling bromine in chloroform, phosphorus pentabromide in hot chloroform or carbon disulfide, liquid bromine without a solvent, dilute or concentrated hydrochloric acid, dilute nitric acid, saturated sodium hydrogen sulfide.

The Acetyl Derivative.—One and two-tenths grams of the white oxidation product was covered with acetyl chloride, 2 drops of concd. sulfuric acid added and the mixture heated gently in an acetylation flask for three hours. Fumes of hydrogen chloride were evolved from the start. The contents of the flask, poured into 200 cc. of ice water, gave 1.1 g. of the white acetyl derivative. Three recrystallizations from dilute ethyl alcohol gave a pure white product, m. p. 141–144° (decomp.). A sample recrystallized twice more was used for analysis.

Anal. Subs., 0.1261, 0.1889: AgBr, 0.1437, 0.2146. Subs., 0.1861, 0.1655: CO_2, 0.1964, 0.1743; H_2O, 0.0345, 0.0315. Calcd. for $C_{16}H_{12}O_9Br_4$: C, 28.45; H, 1.81; Br, 47.91. Found: C, 28.78, 28.72; H, 2.07, 2.13; Br, 48.16, 48.34.

The same acetyl derivative is obtained by using acetic anhydride and glacial acetic acid as the acetylating agent. It crystallizes from dilute alcohol in minute, colorless needles. It is moderately soluble in ethyl alcohol, methyl alcohol, glacial acetic acid, chloroform and carbon disulfide; slightly soluble in fractol or ligroin.

Action of Dilute Alkali upon the Acetyl Derivative.—A sample of the acetyl derivative, when boiled with 6% potassium hydroxide, slowly went into solution. When the solution was cooled and acidified with a few drops of concentrated hydrochloric acid, a white material precipitated, which was shown, by the method of mixed melting points, to be tribromopyrogallol-2,6-dimethyl ether.

The Action of Dilute Alkali upon the Colorless Oxidation Product.—An example is given of one of the hydrolytic experiments in which quantitative technique was adopted. Ninety-eight hundredths gram of the pure colorless oxidation compound was dissolved in 90 cc. of cold 6% potassium hydroxide. Solution required only a minute or two. Immediate acidification at this point would give a good yield of the tribromodimethoxyphenol; however, for the sake of quantitative results, the solution was heated gently on the steam-bath for two hours, then nearly neutralized with glacial acetic acid and made slightly acid with dilute (1 normal) acetic acid. The precipitate which resulted was allowed to stand overnight, then filtered onto a weighed Gooch crucible and dried over calcium chloride in a vacuum desiccator. The tribromopyrogallol-2,6-dimethyl ether weighed 0.62 g., or 63.3% of the weight of the starting material. A check determination gave 63.2%.

A sample of the phenol thus prepared was crystallized twice from dilute ethyl alcohol, giving pure white, delicate needles, m. p. 133.8–134.0°; mixed melting point with a known sample of tribromopyrogallol-2,6-dimethyl ether, 134–134.2°. Since it was exceedingly important to establish, without question, the identity of this material, the purified material was subjected to analysis.

Anal. Subs., 0.2002, 0.2037: AgBr (Carius), 0.2881, 0.2943. Subs., 0.0695, 0.0925: CO_2, 0.0664, 0.0841: H_2O, 0.0151, 0.0177. Calcd. for $C_6H_7O_3Br_3$: Br, 61.34; C, 24.87; H, 1.80. Found: Br, 61.24, 61.48; C, 25.00, 24.80; H, 2.35, 2.15.

Investigation of the Filtrate from the Hydrolysis Reaction.—Examination of the solution from which the tribromopyrogallol-dimethyl ether was filtered led to the following results. Silver nitrate and concd. nitric acid gave a heavy precipitate of silver bromide, showing that further decomposition occurred when the phenol was split off.

Chlorine water and chloroform also disclosed the presence of much free bromide ion. From the filtrate from one sample of 0.57 g. of the white oxidation product, 0.25 g. of silver bromide, equivalent to 0.10 g. of bromine or 33% of the total bromine present in the starting material, was obtained. This, plus the bromine content of the dimethyl ether, accounts for approximately the total bromine available. Another portion of the solution, when neutralized with ammonia and treated with a solution of calcium chloride, gave a white precipitate which gradually darkened on standing, indicating the presence of some reducing acid residue. This was confirmed by the fact that permanganate acidified with dilute sulfuric acid was rapidly decolorized.

The filtrate from one hydrolytic experiment was extracted with ether and the ether extracts allowed to evaporate. There was obtained less than 0.1 g. of an impure white material, melting at 150–160°. The substance was exceedingly deliquescent; standing in the air for even a few moments rendered it of a sirupy consistency. It could not again be isolated, even in this state of impurity, although several attempts were made to do so.

Hydrolytic Decomposition by Means of Other Alkalies.—The hydrolysis could be effected by the use of weaker bases than potassium hydroxide, for example, ammonia or aniline. The latter reagent had previously been used in attempts to obtain an anilide of the colorless compound, without success. It was now clear why these experiments had proved fruitless. If heated for a few minutes with aniline in alcoholic solution, the substance was unaffected. If heated for a somewhat longer time, a gummy product resulted, from which a quantity of the tribromodimethoxyphenol could be obtained. The effect of aniline when used without a solvent was either to leave the colorless material unaffected, or to cause deep-seated decomposition of the substance.

Oxidation of 3,5-Dibromo-6-methoxy-2-(3,4,5-tribromo-2,6-dimethoxyphenoxyl)-p-benzoquinone.—A sample of the above compound, obtained as a by-product during the oxidation of tribromopyrogallol-2,6-dimethyl ether to the colorless oxidation product, was recrystallized three times from glacial acetic acid. It melted at 219–219.5° (Hunter and Levine report 214°). When recrystallized again it melted at 219.5° sharply. Thirty-five hundredths gram of this material was suspended in 50 cc. of 50% acetic acid, heated to 80° and 0.2 g. of chromium trioxide added. The heating was continued for one and one-half hours, after which the solution was cooled and the unchanged quinone filtered. The filtrate was diluted with 120 cc. of water. A white substance slowly precipitated. After being filtered, washed and dried at 100°, it showed a melting point of 200.5–201.5° (only the most highly purified samples of the white product melt above this temperature) with decomposition, and was found to be identical with the white oxidation product obtained in the original oxidation experiments.

Oxidation of Trichloropyrogallol-2,6-dimethyl Ether.—A representative procedure was as follows. Three grams of trichloropyrogallol-2,6-dimethyl ether was dissolved in 350 cc. of 50% acetic acid and heated on a water-bath to 78°. Two grams (1.7 molar equivalents) of chromium trioxide was stirred in and the heating continued for ten to fifteen minutes, after which the mixture was cooled and the red phenoxyquinone filtered off. (As in the case of the corresponding bromo compound, this phenoxyquinone usually precipitated immediately upon addition of the oxidant, but it varied in amount, and in one or two cases it failed to appear at all.) The filtrate was poured into 500 cc. of cold water and allowed to stand overnight, when the white oxidation product had settled to the bottom of the beaker. Most of the supernatant liquid was decanted, and the precipitate was filtered onto a fluted filter paper, washed with dilute acetic acid, water and dilute alcohol and dried between sheets of filter paper. The average yield of crude material was 31% of the weight of the starting material. The crude material melted at 177–182° (decomp.). After crystallizing twice from dilute acetic acid, twice from dilute ethyl alcohol and twice from dilute methyl alcohol, it melted at 187.4–187.8°, with decomposition.

Anal. Subs., 0.1059, 0.1003, 0.1391, 0 1270: AgCl (Carius), 0.1380, 0.1284, 0.1779, 0.1627. Subs., 0 1657, 0.1669: CO_2, 0.2300, 0.2297; H_2O, 0.0357, 0.0365. Subs., 0.2040, 0.2027: AgI (Zeisel), 0.3220, 0.3175. Calcd. for $C_{14}H_{10}O_8Cl_4$ (3 OCH_3): Cl, 31.65; C, 37.53; H, 2.25; 0, 28.57; OCH_3, 20.76; mol. wt., 448. Found: Cl, 32.24, 31.67, 3164, 31.69; C, 3785, 37.53; H, 2.41, 2.45; O (by difference), 28.10, 28.33; OCH_3, 20.84, 20.68; mol. wt. (in ethylene dibromide), 525, 476, 460; mol. wt. (in camphor), 515.

Properties of the Colorless Oxidation Product of **Trichloropyrogallol-2,6-dimethyl** Ether.—This substance crystallizes from dilute alcohol in small, white, delicate needles, which melt, when very pure, at 187.4–187.8°, with decomposition. The microscopic crystals are much better developed than those of the bromine analog, which gives reason to suspect, *a priori*, a much smaller molecule in the former case than in the latter. It is readily soluble in ethyl alcohol, methyl alcohol, glacial acetic acid, acetone, chloroform and ether; slightly soluble in carbon disulfide, benzene, toluene, xylene and ethylene dibromide; practically insoluble in water, carbon tetrachloride and fractol.[11]

Like the bromine analog, the substance is inert to most common chemical reagents It is unaffected by dilute or concentrated hydrochloric acid, dilute or concentrated nitric acid, saturated sodium hydrogen sulfide, bromine, pure or in solution, and is attacked only very slowly by hot acid or alkaline permanganate. The pure material dissolves in concentrated sulfuric acid to a clear solution One such solution, on dilution, was found to give a precipitate of trichloropyrogallol-2,6-dimethyl ether (m. p, 121–122°) The same substance was produced by the action of 6% potassium hydroxide on the colorless product, and subsequent acidification, by dilute acetic acid, of the solution produced. It was identified by the method of mixed melting points. A large amount of free chloride ion was found to be produced during the hydrolytic reaction, and there was also present in the solution, after reaction, a substance which reduced acid permanganate. It could not be isolated.

Acetylation.—Fifteen-hundredths gram of the colorless compound and 30 cc. of acetic anhydride, contained in a long-necked flask, was warmed gently over a free flame for two to three hours. The contents of the flask were cooled, neutralized with sodium hydroxide and diluted with water. The brown product was crystallized from dilute alcohol, giving white crystals, m. p. 135–136°, with decomposition. A chlorine analysis on the crude product indicated that it was a monoacetyl derivative.

Anal. Calcd. for $C_{16}H_{12}O_9Cl_4$: Cl, 29.0. Found: 27.7, 29.0.

Oxidation **of 3,5-Dichloro-6-methoxy-2-(3,4,5-trichloro-2,6-dimethoxyphenoxyl)-*p*-benzoquinone.**—Five-tenths gram of the above compound was suspended in 100 cc. of 50% acetic acid, and treated at 78° with 0.35 g. of chromium trioxide. After heating at this temperature for one and one-half hours, the solution was cooled, the excess quinone filtered and the filtrate poured into 200 cc. of cold water. After twenty-four hours, the small amount of white material which had settled to the bottom of the vessel was collected, washed with water and dried. It melted at 186–188°, with decomposition, and was identical with the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether.

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[11] The oxidation product sometimes appears in the colloidal condition, either when first precipitated from 50% acetic acid by dilution, or on subsequent recrystallization. Under these circumstances, purification cannot be effected and the material must be discarded.

Summary

The oxidation of halogenated pyrogallol-2,6-dimethyl ethers leads to the formation of colorless products. The same products are likewise obtained by the further oxidation of phenoxy quinones, derived from the halogenated phenols by oxidation. These colorless compounds differ from previously known quinone oxidation products by virtue of the fact that in their formation by rupture of the quinone ring, only one carbon atom of the ring is lost.

Structures are proposed for these compounds, and the mechanism by which they are formed is discussed.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

DERIVATIVES OF PHENYLBORIC ACID, THEIR PREPARATION AND ACTION UPON BACTERIA[1]

BY WILLIAM SEAMAN AND JOHN R. JOHNSON

RECEIVED NOVEMBER 17, 1930 PUBLISHED FEBRUARY 9, 1931

The fact that boric acid acts as a very mild antiseptic agent suggested that, in seeking new types of organic antiseptics, an investigation of the organic boric acids, R-B$(OH)_2$, would be of interest. Michaelis and Becker,[2] who first prepared phenylboric acid, observed that this substance was toxic toward microorganisms and relatively harmless toward higher animals. Notwithstanding the promising indications of this early work, no further investigations have been made upon the antiseptic action of the substituted boric acids. The present study was undertaken with the object of preparing a number of derivatives of phenylboric acid containing nitro and amino groups, and testing their action on microorganisms.

Since none of the usual methods for the preparation of aryl boric acids could be adapted readily to the direct synthesis of the nitrophenylboric acids,[3] it seemed desirable to introduce the nitro group by the nitration of phenylboric acid. This compound is prepared conveniently by the interaction of boron trifluoride[4] or methyl borate[5] and phenylmagnesium bromide.

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[1] This article is an abstract of a thesis submitted by William Seaman to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in March, 1929.

[2] (a) Michaelis and Becker, **Ber.,** 13, 58 (1880); (b) *ibid.,* 15, 180 (1882).

[3] An adaptation of the method of preparation of aryl boric acids used by Michaelis and Becker would involve the interaction of boron trichloride or boron tribromide with a bis-(nitrophenyl)-mercury. Although it has been possible to prepare bis-(m-nitrophenyl)-mercury (unpublished work of R. S. Shelton in this Laboratory), the relative inaccessibility of such compounds led us to seek other methods.

[4] Krause and Nitsche, **Ber.,** 54, 2784 (1921); 55, 1261 (1922); German patent 371,467 [*C. A.,* 18, 992 (1924)].

[5] **(a)** Khotinsky and Melamed, **Ber.,** 42, 3090 (1909); (b) Gilman and Vernon, THIS JOURNAL, 48, 1064 (1926).

After a preliminary study of the nitration of phenylboric acid, two satisfactory methods of procedure were developed, whereby it was possible to produce the three isomeric nitro compounds. The ortho and meta compounds could be prepared in relatively large amounts but the para isomer was only obtained in very small amounts. Nitration at a low temperature, in the presence of acetic anhydride, with a moderate excess of fuming nitric acid gave a mixture containing about 95% of o-nitrophenylboric acid and 5% of *p*-nitrophenylboric acid. The combined products represented yields of about 65% of the theoretical quantities. Nitration with fuming nitric acid alone, at low temperature, led to the production of a mixture of approximately 85% of m-nitrophenylboric acid and 15% of the ortho isomer.[6] The combined products in this case represented about 80% of the theoretical yield. The separation of the isomeric nitrophenylboric acids was accomplished by fractional crystallizations from aqueous solutions.

In order to establish the structure of the three isomeric nitrophenylboric acids, the boric acid residue was replaced by the chloromercuri- group,? and this in turn by bromine

$$NO_2C_6H_4B(OH)_2\ 4\ HgCl_2 + H_2O \longrightarrow NO_2C_6H_4HgCl + HCl + H_3BO_3$$
$$2NO_2C_6H_4HgCl + 2Br_2 \longrightarrow 2NO_2C_6H_4Br + HgCl_2 + HgBr_2$$

Either the nitrophenylmercuric chlorides or the corresponding bromonitrobenzenes were identified by comparison with authentic specimens.

The o- and m-aminophenylboricacids were obtained by reduction of the nitro compounds by means of freshly precipitated ferrous hydroxide.[8] On account of the small amount of *p*-nitrophenylboric acid at our disposal, the para isomer was not reduced. m-Aminophenylboric acid was isolated as a crystalline solid and was converted to the acetyl and benzoyl derivatives. o-Aminophenylboric acid was not isolated as such, but was converted to the corresponding benzoyl derivative.

Since the positions of the nitro group in the nitrophenylboric acids had been established, further proof of the orientation of the groups in the

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[6] Since the preparation of this manuscript, Ainley and Challenger [J.Chem. *Soc* , 2176 (1930)] have described the nitration of phenylboric acid to produce *m*-nitrophenylboric acid. These investigators did not isolate the corresponding ortho and para isomers which are described in the present article, but determined the relative proportions of the isomers produced, by examination of the mixed bromonitrobenzenes obtained from them. Their method undoubtedly gives more accurate data concerning this point, but they have dealt only with the nitration technique in which the meta isomer predominates. Their methods of establishing the position of the nitro group were very similar to those used in this investigation.

[7] Michaelis and Becker, ***Ber.***, 15, 182 (1882).

[8] Subsequently, F. R. Bean, in this Laboratory, has shown that catalytic reduction with the platinum catalyst of Adams and Shriner ("Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. VIII, 1928, p. 92) is a simpler method of effecting this reduction.

amino derivatives was unnecessary. However, in order to confirm the structures of the amino derivatives, it seemed desirable to establish the state of combination of the nitrogen atom. This was accomplished readily by elimination of the boric acid residue,[9] and identification of the resulting nitrogen compound

$$CH_3CONHC_6H_4B(OH)_2 + AgNO_3 + NH_3 \longrightarrow CH_3CONHC_6H_4BO_2HAg + NH_4NO_3$$

$$2CH_3CONHC_6H_4BO_2HAg + 2H_2O \longrightarrow 2CH_3CONHC_6H_5 + 2H_3BO_3 + Ag_2O$$

In the course of this work several attempts were made to devise new methods for the preparation of aromatic boric acids. One of these was an attempt to introduce the boric acid residue directly, by heating aniline with boric acid, in a manner analogous to that used for the preparation of arsanilic acid. It has been shown by Chaudhuri[10] that an anilide of boric acid, $C_6H_5NHB{=}O$, can be obtained by heating aniline with boric acid. None of our efforts to effect a rearrangement of the boric acid group from the side chain into the ring was successful, either with boric anilide or with its acetyl and benzoyl derivatives. Experiments were also made upon the replacement of the sulfinic acid group by the boric acid residue. Sodium benzenesulfinate and *p*-toluenesulfinate were heated with boric acid and with borax, but no trace of an organic boric acid could be observed in the products of these reactions.

Work is now in progress on the preparation of hydroxyphenylboric acids, and of other substituted nitro and amino compounds.

Experimental

Methyl Borate.—For use in the preparation of phenylboric acid, methyl borate should be quite free from methyl alcohol, since the latter caused a marked diminution of the yield, apparently greater than could be accounted for on the basis of the Grignard reagent actually destroyed by the alcohol. Diverse boiling points for methyl borate (from 55 to 72°) are reported in the literature,[11] probably due to the fact that methyl borate forms an azeotropic mixture with methyl alcohol[11d] from which it is relatively difficult to remove the last traces of methyl alcohol. To accomplish this, we employed the method of Schiff,[11b] which consists in washing with cold concd. sulfuric acid. The purified methyl borate obtained thus had the following properties: b. p. 67–67.8° at 750 mm.; d^{20}_{4} 0.932; n^{24}_{D} 1.3558.

Phenylboric Acid, $C_6H_5\text{-}B(OH)_2$.—Preliminary tests showed that the yields of phenylboric acid were improved by adding the phenylmagnesium bromide to an ethereal solution of methyl borate, instead of the reverse procedure used by Khotinsky and

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[9] Michaelis and Becker, *Ber.*, 15, 181 (1882).

[10] Chaudhuri, *J. Chem. Soc.*, 117, 1081 (1920).

[11] (a) Gasselin, *Ann. chim. phys.*, [7] 3, 21 (1894), recorded 55–56"; (b) Schiff, *Ann. Suppl.*, 5, 160, 184 (1867), reported b. p. 65°, sp. gr. 0.940; (c) Ebelmen, *Ann.*, 60, 252 (1846), reported b. p. 72°, sp. gr. 0.955; (d) Lecat, *Ann. soc. sci. Bruxelles*, 47B, I, 63–71 (1927); [*C. A.*, 22, 4296 (1928)]. At the time when this work was started we were not aware of the work of Lecat on the azeotropic mixture, methyl borate + methyl alcohol.

Melamed.[5] Even this modification did not allow us to attain the yields of 50 and 86% which are claimed by previous investigators.[12]

During the course of forty-five minutes, 0.25 mole of phenylmagnesium bromide (in 1 molar solution) was added to a solution of 26 g. (0.25 mole) of methyl borate in 80 cc. of pure ether. The methyl borate solution was maintained at about −12° during this addition, and the reaction mixture was shaken constantly by hand. After all of the Grignard reagent had been added, the reaction mixture was refluxed gently for fifteen minutes. It was then thoroughly chilled in a freezing mixture, and 125 cc. of a cold 1% solution of sulfuric acid was added cautiously. After shaking thoroughly, the ethereal layer was decanted and the aqueous layer was extracted with four 100-cc portions of ether. The combined ethereal solutions were dried and the ether distilled off. The solid residue was crystallized from about 70 cc. of water, with the addition of decolorizing carbon. The average yield of a number of runs was 9 g., which is 30% of the theoretical amount. The product obtained in this way was sufficiently pure to be used for nitration.

For more thorough purification, to obtain specimens for determination of physical constants and for bacteriological tests, the substance was recrystallized from petroleum benzene (b. p. 110–120°). The purified material melted at 215.5–219° by the capillary tube method, in a preheated bath; m. p. 221° (corr.) on the Maquenne block.[13]

Michaelis and Becker[2] reported a melting point of 204" for the sample of phenylboric acid that they tested for antiseptic properties; in a later communication the melting point was recorded as 216°.[15] This discrepancy, together with the fact that they reported that phenylboric acid has a pleasant taste and a phenolic odor, leads us to believe that they did not work with perfectly pure material. Our purified specimens were odorless and tasteless, and showed much less antiseptic action.

The residues from the mother liquors which remained after as much as possible of the phenylboric acid had been recovered, contained a yellow solid which melted incompletely near 300°. This material gave a qualitative test for boron[16] and responded to the usual tests for aromatic boric acids with silver nitrate and with mercuric chloride. This material was not examined further; it may consist in part of diphenylboric acid.[15]

***m*-Nitrophenylboric** Acid.—In an ice–salt freezing mixture, 75 g. of colorless fuming

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[12] More recent work of F. R. Bean, in this Laboratory, using n-butyl borate and effecting the reaction at a temperature of −50 to −60°, gave yields of 50–60% of the theoretical.

[13] The capillary tube melting points of the aromatic boric acids were found to be greatly influenced by the manner of heating, since the substances are capable of undergoing dehydration and other decomposition in the course of heating. The melting points of these substances are much more characteristic and more constant if the Maquenne block [Houben–Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, **1921,** Vol. I, pp. 734–735] is used, so that preliminary heating is avoided. Since the melting points observed on the Maquenne block frequently differ from those obtained by the usual methods, the values are not directly comparable. In Table I, at the end of the experimental section, are tabulated the various melting points of the principal compounds described in this article. A very convenient and elegant modification of the Maquenne block has been devised in this Laboratory.[14]

[14] Dennis and Shelton, THIS JOURNAL, 52, 3128 (1930).

[15] Michaelis and Behrens, *Ber.*, **27,** 244 (1894).

[16] Two qualitative tests for boron were used in connection with this work: (1) observation of the green color imparted to a Bunsen flame when the compounds were burned upon a foil, and *(2)* fusion with metallic sodium, treating with slightly acidulated water and testing the solution with turmeric paper.

nitric acid (sp. gr. 1.50), to which a little urea had been added, was cooled to −15°. During one and one-half hours, 10 g. of finely powdered, dry phenylboric acid was added, with good mechanical stirring, so that the temperature did not rise above −9° The mixture was stirred for ten minutes after all the phenylboric acid had been added, and was then poured onto 50 g. of ice.[17] The precipitated nitrophenylboric acid (I) was filtered with suction, and recrystallized from *a* small volume of water, with the addition of decolorizing carbon.

The original filtrate was cooled in an ice-bath, neutralized to congo red with strong sodium hydroxide solution, and then slightly acidulated with nitric acid. The solution was extracted thoroughly with ether, and the solvent evaporated off at room temperature. The residue was fractionally crystallized from a small volume of water, with the addition of decolorizing carbon. The crystals (II) which separated before the solution had cooled completely (30°) consisted chiefly of m-nitrophenylboric acid, and were combined with the original precipitate (I) and subjected to further purification. The substance which crystallized upon cooling the filtrate from II, in an ice-bath, consisted largely of o-nitrophenylboric acid. The latter was purified by crystallization from a very small volume of water. The average yield of m-nitrophenylboric was 10 g. (70% of the theoretical); that of o-nitrophenylboric acid was 1.5 g. (10% of the theoretical).

***m*-Nitrophenylboric** Acid.—This substance forms yellow prismatic crystals. It is slightly soluble in cold water, moderately soluble in hot water, soluble in alcohol and ether. It dissolves in aqueous sodium hydroxide, sodium carbonate and ammonia. It gives the characteristic tests for aromatic boric acids with silver nitrate and with mercuric chloride, and the usual qualitative tests for boron. The air-dried purified m-nitrophenylboric acid melted with charring at 275–276.5° (corr.) in a capillary tube placed in a bath preheated to about 250°, and at 273" (corr.) in a bath which was not preheated.[18] On the Maquenne block the melting point was 319° (corr.).

After drying to constant weight in a desiccator, the substance melted with charring at 285–286° (corr.) in a bath not preheated. This is evidently the melting point of the anhydride, $NO_2C_6H_4B{=}O$, since the analytical data on this sample agreed with the theoretical values for the anhydride. All samples for analysis were dried in *vacuo* over concd. sulfuric acid.[19]

Anal. Calcd. for $NO_2C_6H_4BO$: C, 48.37; N, 9.41. Calcd. for $NO_2C_6H_4B(OH)_2$: C, 43.14; N, 8.39. Found: C, 48.05, 48.17; N, 9.90, 9.75.

Determination of the Position of the Nitro Group.—A hot aqueous solution of 1 g. of the nitrophenylboric acid was treated with a concd. aqueous solution of 1.8 g. of mercuric chloride. The resulting precipitate of nitrophenylmercuric chloride was washed with water, and treated with an excess of a solution of bromine in aqueous potassium bromide. The mixture was shaken for two and one-half hours at room temperature and extracted with ether. The residue, after removal of the solvent, was washed free from bromine and recrystallized from 50% alcohol; m. p. 53.7–54.2° (corr.). An authentic specimen of m-bromonitrobenzene (Kahlbaum), used for comparison,

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[17] A small amount of nitrobenzene is always formed in these nitrations; if the reaction is carried out at higher temperatures, nitrobenzene and boric acid are produced as the principal products.

[18] Ainley and Challenger, Ref. 6, report m. p. 273° for m-nitrophenylboric acid, but do not state the conditions of the melting point determination.

[19] Carbon determinations were made by the Parr total carbon method, which did not prove entirely satisfactory. Ainley and Challenger (Ref. 6) reported that the usual combustion method gave very low results for carbon. The nitrogen determinations were made by the Dumas method,

melted at 54.0–54.2° (corr.); a mixture of the two substances melted at 53.7–54.2° (corr.). The formation of m-bromonitrobenzene establishes the structure of the above acid as m-nitrophenylboric acid.

o-Nitrophenylboric Acid.—Six grams of colorless fuming nitric acid (sp. gr. 1.50), to which a few crystals of urea had been added, was allowed to drop slowly into a suspension of 10 g. of phenylboric acid in 90 cc. of acetic anhydride, cooled to −15°. Mechanical stirring was used throughout the addition, which required about forty-five minutes, and the mixture was stirred for about one and one-half hours after all of the nitric acid had been added. During this period the temperature was allowed to rise slowly to −7°; the freezing-bath was then removed and the stirring was continued until all of the acid had dissolved (about one hour). Occasional cooling was used to keep the temperature below +20°. The reaction mixture was poured slowly into 200 cc. of ice water and the whole was agitated until a clear homogeneous solution was obtained. The solution was concentrated to a small volume at 50°, under reduced pressure; 100 cc. of water was added and the concentration repeated.[20] After cooling, and standing for ten to twelve hours, about 0.3 g. of a crystalline nitrophenylboric acid (III) separated. This was removed by filtration and reserved for examination (see below, *p*-nitrophenylboric acid). The quantity of this product was about 2% of the theoretical yield.

The filtrate was concentrated further, at 50° under reduced pressure, with repeated additions of water, until most of the acetic acid was removed and crystals had separated in the solution. These were separated by filtration, and the mother liquor was concentrated further, until it was reduced to a very small volume After separating the crystals, the final filtrate was made alkaline to congo red with sodium carbonate, slightly acidified with hydrochloric acid, and extracted with ether. Evaporation of the ether extract gave a residue which was combined with the main fractions of *o*-nitrophenylboric acid and recrystallized from a very small amount of water. Approximately 8 g. of crude o-nitrophenylboric acid was obtained (60% of the calculated quantity). This product was sufficiently pure for subsequent syntheses; for further purification the acid was washed with hot carbon tetrachloride and recrystallized from water.

o-Nitrophenylboric acid crystallizes from water in yellow needles. It is moderately soluble in water; soluble in alcohol and ether. o-Nitrophenylboric acid dissolves in aqueous solutions of sodium hydroxide, sodium carbonate and ammonia; it gives the usual qualitative tests for boron. The air-dried substance melted at 139.2–140.8° (corr.), with darkening, in a bath heated from 20°; m. p. 138.7–139.2' (corr.), in a bath preheated to 120°; m. p. 147.5' on the Maquenne block. After drying to constant weight in a vacuum desiccator, over sulfuric acid, the substance melted at 143.5–147.7' (corr.), in a preheated bath. The vacuum dried substance, evidently the anhydride $NO_2C_6H_4B{=}O$, was analyzed.

Anal. Calcd. for $NO_2C_6H_4BO$: C, 48.37; N, 9.41. Calcd. for $NO_2C_6H_4B(OH)_2$: *C*, 43.14; N, 8.39. Found: C (Parr bomb),[21] 46.14, 45.97; N (Dumas), 9.26, 9.62.

Determination of the Position of the Nitro Group.—A hot aqueous solution of 0.38 g. of the above acid was treated with a concd. solution of 0.62 g. of mercuric chloride and heated for five minutes. The resulting nitrophenylmercuric chloride was removed by filtration and crystallized three times from alcohol; m. p. 183.4–184.5" (corr.). An

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[20] During this process a small quantity of a green oil, possibly a nitroso compound, distilled over. The quantity of the material was too small for identification.

[21] The results for carbon are undoubtedly low, since it seemed impossible to achieve a complete combustion in the Parr peroxide bomb. There were always a few specks of unoxidized carbonaceous matter in the fused mass.

authentic specimen of o-nitrophenylmercuric chloride, prepared according to the method of Dimroth,[22] melted at 181.3–183.4° (corr.); a mixture of the two substances melted at 183.4–184.5° (corr.).

***p*-Nitrophenylboric Acid.**— The less soluble fractions (III) of the acid obtained from the nitrations in acetic anhydride were combined and recrystallized from water, with the addition of decolorizing carbon. As a very small amount of this compound was obtained, no analyses were made as it seemed more essential to establish the structure of the compound by conversion to a known compound, and to reserve the remainder for a bacteriological test. The substance gives the usual qualitative tests for boron and for nitrogen.

p-Nitrophenylboric acid crystallizes from water in long, slender, yellow needles. It is slightly soluble in cold water, and is the least soluble of the three isomers; it is soluble in hot water, alcohol and ether. Like the other acids, it dissolves in aqueous solutions of sodium hydroxide, sodium carbonate and ammonia. *p*-Nitrophenylboric acid melts, with decomposition and charring, at 305° (corr.) in a capillary tube in a bath heated from 20°; on the Maquenne block the substance did not melt up to 360°.

Determination of the Position of the Nitro Group.—By the method given for *m*-nitrophenylboric acid, 0.2 g. of the nitrophenylboric acid described above was converted to a bromonitrobenzene. The latter, after crystallization from 50% alcohol melted at 122.8–124.4° (corr.). An authentic specimen of p-bromonitrobenzene (Kahlbaum) melted at 126.4–127.4° (corr.); a mixture of the two substances melted at 125.9–126.9° (corr.).

m-Aminophenylboric Acid.—Reduction of the nitro acids was effected by the use of freshly precipitated ferrous hydroxide, according to a modification of the procedure of Claisen and Thompson, and Jacobs, Heidelberger and Rolf.[23]

In a 1-liter flask (or bottle), 71 g. of ferrous sulfate crystals (95% $FeSO_4 \cdot 7H_2O$ as determined by titration) was dissolved in 250 cc. of air-free water; a suspension of 81 g. of hydrated barium hydroxide ($Ba(OH)_2 \cdot 8H_2O$) in 150 cc. of water was added in several portions, the mixture was shaken thoroughly until it reacted alkaline to litmus, and a uniform suspension of ferrous hydroxide was obtained. A uniform suspension of 12 g. of hydrated barium hydroxide and 6 g. of m-nitrophenylboric acid in 125 cc. of air-free water was added in one portion to the ferrous hydroxide, and the mixture was shaken vigorously for ten minutes, during which the green color of the ferrous hydroxide changed to the brown of ferric hydroxide. The insoluble material was filtered off with suction, suspended in water and washed thoroughly. The filtrate and washings were united and the barium ions were removed by exact precipitation with sulfuric acid, so that a test portion of the filtered solution gave no turbidity with either sulfuric acid or barium hydroxide solution. The filtered solution was concentrated at 50°, under reduced pressure, in an atmosphere of nitrogen. The resulting yellow crystals of the crude m-aminophenylboric acid were manipulated, as far as practicable, in an inert atmosphere. The filtrate from the main crop of crystals could be concentrated further to obtain a small additional quantity of the amino acid; it proved more satisfactory, however, to make use of this solution for the preparation of the benzoyl derivative. The yield of crude m-aminophenylboric acid was 2.2–2.4 g. (44–48%), and 0.3–0.5 g. of the benzoyl derivative was obtained from the mother liquors. The crude amino acid was recrystallized from a very small volume of water (in an atmosphere of nitrogen), with the addition of decolorizing carbon. The purified product formed pale yellow hexagonal plates; the slight tinge of color could not be removed by several recrystallizations.

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[22] Dimroth, *Ber.*, 35, 2036 (1902).

[23] (a) Claisen and Thompson, *ibid.*, 12, 1946 (1879); (b) Jacobs, Heidelberger and Rolf, THIS JOURNAL, 40, 1580 (1918).

Undoubtedly the pure compound is colorless; the color of our product was probably due to the merest traces of impurity, since the substance had a fairly sharp melting point. In a capillary tube, either from a bath at 20° or a preheated bath, the substance melted at 92.8–93.8° (corr.), and resolidified if kept just above this temperature; upon further heating, the compound melted indefinitely, with darkening, near 200°. On the Maquenne block the material melted sharply at 176° (corr.). *m*-Aminophenylboric acid is soluble in water and alcohol, sparingly soluble in ether.

For analysis the substance was dried to constant weight in a vacuum desiccator (ten days) over sulfuric acid. After drying the melting point was 193" (corr.) on the Maquenne block; the dried substance melted indefinitely at about 168° (with darkening), in a capillary tube in a bath heated from 20°.

Anal. Calcd. for $NH_2C_6H_4B(OH)_2$: N, 10.23. Calcd. for $NH_2C_6H_4BO$: N, 11.78. Calcd. for $(NH_2C_6H_4BOH)_2O$: N, 10.95. Found: (Kjeldahl) N, 11.11, 11.12.

The nitrogen determinations indicated that the completely dried sample was an anhydride formed by the elimination of one molecule of water from two molecules of the acid.[24] The air-dried substance was undoubtedly the acid and not an anhydride, since it dissolved immediately in water and gave the typical tests for aromatic boric acids. Experience with the anhydrides of various boric acids indicates that the anhydrides do not react at once with cold water to regenerate the acids.

Since the position of the amino group was established by the relationship to *m*-nitrophenylboric acid, m-aminophenylboric acid was characterized merely by conversion to the acetyl and benzoyl derivatives, and by the identification of aniline after removal of the boric acid residue.

Elimination of the Boric Acid Residue.—To a slightly ammoniacal aqueous solution of 0.2 g. of the substance, an excess of 5% aqueous silver nitrate solution was added; the resulting precipitate of the silver salt was filtered and washed with water. This was suspended in water and boiled gently for fifteen minutes to remove completely the boric acid group, and the aniline was recovered by steam distillation. Aniline was identified by the following tests: (1) development of a transient violet color with calcium hypochlorite solution; (2) formation of a colorless precipitate with bromine water; (3) conversion to an alkali-soluble benzene sulfonamide, m. p. 107.3–110.3" (corr.), which showed no depression of the melting point when mixed with an authentic specimen of benzenesulfonanilide, m. p. 109.3–111.3° (corr.).

Acetyl-m-aminophenylboric Acid.—A solution of the amino acid obtained by the reduction of 6.8 g. of m-nitrophenylboric acid was evaporated almost to dryness and treated with 25 g. of acetic anhydride. The mixture became warm and the solid particles dissolved. The acetic acid was removed by distillation at 50°, in an atmosphere of nitrogen, by addition of small portions of water and repeated evaporations. The acetyl derivative separated from the solution as the acetic acid was removed. The first crop of crystals, amounting to 2.2 g., was colorless; an additional amount, 1.5 g., of a slightly colored product was recovered from the mother liquors. Both fractions were purified by recrystallization from a small volume of hot water, with the addition of decolorizing carbon. The total yield of the crude product was 3.7 g., which is 56% of the theoretical amount calculated from the m-nitrophenylboric acid.

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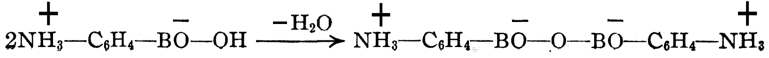
[24] An explanation of the formation of this type of anhydride is that the amino acid may exist as a salt (as do glycine and sulfanilic acid) formed by intramolecular neutralization; thus, the elimination of a molecule of water can only occur between two molecules:



$$2\overset{+}{N}H_3—C_6H_4—B\overset{-}{O}—OH \xrightarrow{-H_2O} \overset{+}{N}H_3—C_6H_4—B\overset{-}{O}—O—B\overset{-}{O}—C_6H_4—\overset{+}{N}H_3$$

Acetyl-*m*-aminophenylboric acid crystallizes from water in colorless prismatic plates; it is moderately soluble in water, alcohol and ethyl acetate, but almost insoluble in ether. It dissolves in aqueous alkalies. In a capillary tube the substance melted, with darkening, at 274–275° (corr.) when heated from 20°. On the Maquenne block the compound melted and immediately resolidified, without decomposition, at about 160°. The transition temperature could not be determined accurately, as only the smallest particles (viewed through a magnifying glass) could be seen to melt completely and the resolidification was almost instantaneous. The air-dried product lost no appreciable weight in a vacuum desiccator over sulfuric acid.

Anal. Calcd. for $C_8H_{10}O_3NB$: N, **7.83.** Found: (Kjeldahl) N, **7.72, 7.64.**

The acid gives the usual qualitative tests for boron, and the characteristic precipitates with aqueous solutions of mercuric chloride and of silver nitrate. Elimination of the boric acid group, effected by heating the silver salt in water, gave acetanilide, m. p. **112.3–114.3** (corr.), identified by comparison with an authentic specimen.

Benzoyl-*m*-aminophenylboric Acid.—A concd. solution of the amino acid obtained by the reduction of **2.0** g. of m-nitrophenylboric acid was treated with **2** g. of sodium bicarbonate and benzoylated with **2** g. of benzoyl chloride. The crude pale yellow benzoyl derivative weighed **1.2** g. **(42%** of the theoretical yield, based on the nitro acid). A preliminary purification was effected by dissolving the crude acid in dilute alkali, filtering and reprecipitating by pouring into dilute hydrochloric acid. A final purification was made by crystallization from 30% alcohol, with the addition of decolorizing carbon.

Benzoyl-*m*-aminophenylboric acid crystallizes from dilute alcohol in colorless prisms; it is almost insoluble in cold water and in ether, soluble in hot water and in alcohol. It is completely soluble in dilute sodium hydroxide solutions but only slightly soluble in sodium bicarbonate and sodium carbonate solutions. The air-dried substance melted in *a* capillary tube, with darkening, at 290° (corr.) in a bath heated from 20°; on the Maquenne block the substance melted with immediate resolidification, at about **200"** (co.). As the behavior of this compound was very similar to that of the acetyl derivative, it was not possible to determine accurately the temperature of the transition point. An air-dried sample did not lose weight in a vacuum desiccator over sulfuric acid.

Anal. Calcd. for $C_{13}H_{12}O_3NB$: N, **5.82.** Found: (Kjeldahl) **N, 5.59, 5.80.**

This acid gives the usual qualitative tests for boron, and the characteristic precipitates with aqueous solutions of mercuric chloride and of silver nitrate. Elimination of the boric acid group, effected by heating the silver salt in water, gave benzanilide, m. p. 163.3–164.4° (corr.), which was identified by comparison with an authentic sample. Hydrolysis with hot concd. aqueous sodium hydroxide (one and one-half hours) gave benzoic acid, m. p. 121.3–122.3° (corr.). An attempt to hydrolyze the benzoyl derivative by boiling for one-half hour with strong potassium hydroxide in 90% alcohol was unsuccessful.

Benzoyl-o-aminophenylboric Acid.—Although several attempts to isolate o-aminophenylboric acid and its acetyl derivative were unsuccessful,[25] it was possible to obtain benzoyl-o-aminophenylboric acid. o-Nitrophenylboric acid was reduced by the same general procedure as the meta isomer, except that the reduction was effected at 95–

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[25] Our experiments indicate that o-aminophenylboric acid must be present in the solution obtained by reducing o-nitrophenylboric acid. Attempts to isolate the o-amino compound yielded phenylboric acid, due evidently to a reductive deamination; phenylboric acid was isolated likewise when the crude reduction product was treated with acetic anhydride in an effort to obtain the acetyl derivative. In one experiment, after treatment with acetic anhydride, a small amount of boric acid was isolated.

100°, and the reaction mixture was boiled gently for five minutes before filtering off the precipitated ferric hydroxide and barium sulfate. The filtrate, containing the excess of barium hydroxide, was divided into three portions for benzoylation. Each portion was treated with **1** g. of solid sodium bicarbonate and 1 g. of benzoyl chloride, and shaken thoroughly until there was no odor of benzoyl chloride. Upon acidifying with hydrochloric acid, the crude benzoyl derivative separated in yellow crystals. The yield was **1.6** g. from **3** g. of the nitro acid (37% of the theoretical). The crude product was purified by crystallization from 30% alcohol, with the addition of decolorizing carbon.

Benzoyl-o-aminophenylboric acid crystallizes from dilute alcohol in colorless, transparent platelets. It is very slightly soluble in cold water and ether, soluble in hot water and alcohol. It dissolves completely in dilute sodium hydroxide solution, but not in sodium carbonate or bicarbonate solutions. It gives the usual qualitative tests for nitrogen and boron, and the characteristic tests with mercuric chloride and with silver nitrate solutions. In a capillary tube, immersed in a bath preheated to 200°, the substance melts with darkening at 283–284° (corr.); on the Maquenne block the melting point was **319.5°** (corr.), with darkening. The air-dried product did not lose weight in a vacuum desiccator over sulfuric acid.

Anal. Calcd. for $C_{13}H_{12}O_3NB$: N, **5.82.** Found: (Kjeldahl) **N, 5.92, 5.92.**

The compound was characterized by elimination of the boric acid residue in the usual way. The boron-free product, m. p. 161.5–162° (corr.), was identified as benzanilide.

TABLE I

MELTING POINTS OF SUBSTITUTED BORIC ACIDS

Substituted boric acid, $-B(OH)_2$	M. p., °C. (corr.), capillary tube method From bath at 20°	 From preheated bath[a]	M. p., °C. (corr.), Maquenne block
Phenyl	**210.6–212.6**	**215.5–219.4**	**221**
m-Nitrophenyl	**273** (dec.)	**275–276.5** (dec.)	**319** (dec.)
o-Nitrophenyl	**139.2–140.8**	**138.7–139.2**	**147.5**
p-Nitrophenyl	**305.5** (dec.)	....	Above **360**
m-Aminophenyl	92.8–93.8[b]	**92.8–93.8**[b]	**176**
Acetyl-m-aminophenyl	**274–275**	....	*circa* **170**[b]
Benzoyl-m-aminophenyl	**290**	....	*circa* **200**[b]
Benzoyl-o-aminophenyl	....	**283–284**	**319.5**

[a] In these determinations the bath was heated to a temperature about 10° below the melting point, before immersion of the capillary tube. [b] Resolidifies.

Bacteriological Tests[26]

For the bacteriological tests the substances to be examined were prepared in a high state of purity, as evidenced by constant melting points after repeated crystallizations and homogeneous appearance under the microscope. The first experiments were made with *Staphylococcus aureus*, using the Reddish test. Five cc. of the antiseptic in the dilution noted, was added to 0.5 cc. of a twenty-four hour bouillon culture of *Staphylococcus aureus*. This *Staphylococcus aureus* when tested against phenol should be

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[26] The authors wish to express their thanks to Dr. E. H. Volwiler, Chemical Director, and to Dr. J. F. Biehn, Director of the Department of Clinical Research, of the Abbott Laboratories, North Chicago, Illinois, for their kind cooperation in carrying out the bacteriological tests described in this communication.

killed by a 1:70 dilution in ten minutes, and may or may not be killed by a 1:60 dilution in five minutes.[27]

The following compounds were tested in aqueous solution at a dilution of 1:1000: phenylboric acid, o- and m-nitrophenylboric acids sodium *m*-aminophenylborate, sodium benzoyl-m-aminophenylborate and sodium benzoyl-o-aminophenylborate The results were entirely negative, since the organisms were not killed by any of these solutions, even after fifteen minutes. Similar experiments were made using *B. typhosus* in place of *Staphylococcus*, and the following compounds were tested, at dilutions of 1:1000: boric anilide ($C_6H_5NHB{=}O$), acetyl-m-aminophenylboric acid, and *p*-nitrophenylboric acid; phenylboric acid and boric acid itself were tested at concentrations of 1:200. In this series the tests were allowed to run for two hours. The only positive result was obtained with phenylboric acid (1:200), which killed the organisms within one hour.

Since the preliminary tests indicated a much weaker action than had been anticipated, a milder test was used to enable us to determine the effect of various substituents upon the bacteriostatic action of phenylboric acid. For this purpose the following modified technique was used. To 5 cc. of the test solution were added 5 cc. of plain bouillon and 0.1 cc. of a bouillon culture of Staphylococcus aureus. These cultures were incubated for forty-eight hours, after which they were examined to determine whether or not a bacteriostatic effect[28] had been produced. The results of these tests, shown in Table II, led us to make a more complete examination of three compounds (phenylboric acid, m-nitrophenylboric acid, and *m*-aminophenylboric acid), against *Staphylococcus* aureus. The same modified technique for bacteriostatic action was used, and the following results were obtained: (1) phenylboric acid shqwed bacteriostatic action in dilutions of 1:400 to 1:450, but not at dilutions from 1:475 to 1:1500; (2) *m*-nitrophenylboric acid showed bacteriostatic action in dilutions of 1:500 to 1:2400, but not at a dilution of 1:3200; (3) m-aminophenylboric acid showed no bacteriostatic action in dilutions ranging from 1:400 to 1:3200.

Solutions of these three compounds were also tested in concentrations of 1:200, using 5 cc. of the test solution and 0.1 cc. of a twenty-four hour bouillon culture of Bacillus *typhosus*. m-Nitrophenylboric acid killed these organisms within five minutes, phenylboric acid in ninety minutes and m-aminophenylboric acid did not kill them within two hours.

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[27] To be labeled as an antiseptic solution, under the ruling of the Bureau of Chemistry, the antiseptic solution in the dilution recommended, must kill this *Staphylococcus* culture, under the conditions of the above test, in five minutes.

[28] A bacteriostatic effect is commonly called an antiseptic effect. According to a ruling of the U. S. Department of Agriculture, the terms antiseptic and germicide are synonymous, and the previously stated definition of antiseptic is employed. The term bacteriostatic denotes the property of hindering the growth of organisms without killing them.

TABLE II

TESTS FOR BACTERIOSTATIC ACTION

Substance	Dilution[a]	Result[b]
Phenylboric acid	1:2000	−
m-Nitrophenylboric acid	1:2000	+
o-Nitrophenylboric acid	1:2000	+
p-Nitrophenylboric acid	1:2000	+
Sodium m-aminophenylborate	1:2000	−
Sodium benzoyl-m-aminophenylborate	1:2000	
Sodium benzoyl-o-aminophenylborate	1:2000	
Acetyl-m-aminophenylboric acid	1:2000	
Boric anilide	1:2000	
Phenylboric acid	1:400	+
Boric acid	1:400	−
Boric acid	1:50	+
Control	..	−

[a] Five cc. of the test solution was mixed with 5 cc. of bouillon and 0.1 cc. of a culture of Staphylococcus aureus, and incubated for forty-eight hours.

[b] A minus sign indicates continued development of the organisms; a plus sign denotes arrested development (bacteriostatic action).

Discussion of Bacteriological Tests

It appears that the claims of Michaelis and Becker[2] for the antiseptic efficacy of phenylboric acid were exaggerated. Aside from the question of purity of the phenylboric acid used in their work, it should be pointed out that their tests were made on heterogeneous mixtures of bacteria of unknown vitality, whereas our samples were tested on pure cultures by means of a standardized procedure.

Although none of the substances examined was found to be a powerful antiseptic, several of them possessed marked bacteriostatic properties. The introduction of an amino group (in the meta position) into the molecule of phenylboric acid resulted in a practically complete loss of bacteriostatic action, while the introduction of a nitro group markedly increased the bacteriostatic action.[29]

The fact that phenylboric acid and the derivatives here reported do not act as general antiseptics, does not preclude the possibility that they may have a specific action on certain organisms. This point remains to be tested. Since some of these compounds are soluble both in ether and in water, they may be expected to possess good penetrating power. It is possible that the introduction of a more powerfully antiseptic group (such as a phenolic hydroxyl) into the aromatic boric acid may prove fruitful, since the phenylboric acid residue may serve to give the molecule a satisfactory penetrating power.

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[29] This effect of the nitro group is to be expected, since the nitrophenols are more powerful antiseptics than phenol [Morgan and Cooper, Orig. Corn. 8th Intern. Congr. Appl. Chem., 19,243 (1912); C. A., 6,2944 (1912)].

Summary

Phenylboric acid was prepared in a pure state, and the three isomeric nitrophenylboric acids were obtained from this acid by nitration under appropriate conditions. m-Aminophenylboric acid, its acetyl and benzoyl derivatives, and the benzoyl derivative of o-aminophenylboric acid were prepared. The physical characteristics of these substances are reported.

Bacteriological tests showed that phenylboric acid and the three nitrophenylboric acids exert a bacteriostatic effect upon *Staphylococcus aureus;* m-aminophenylboric acid and its derivatives do not produce a bacteriostatic effect.

The nitrophenylboric acids are more highly bacteriostatic than phenylboric acid, which in turn is much more effective than boric acid. Although no direct comparison was made, it appears that *m*-nitrophenylboric acid (1: 200) approaches or slightly surpasses phenol (1: 70) in its bactericidal action toward B. *typhosus,* but phenylboric acid (1:200) is much weaker than phenol (1: 70).

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

THE EFFECT OF ETHYLENE UPON THE HYDROLYSIS OF SALICIN BY EMULSIN

BY D. T. ENGLIS AND F. A. DYKINS

RECEIVED NOVEMBER 19, 1930 PUBLISHED FEBRUARY 9, 1931

The nature of the transformations brought about by the use of ethylene in the preparation of fruits and vegetables for marketing and the mechanism of the action continue to attract attention. It is generally believed that the changes produced are due to acceleration of enzymic activity. In an earlier paper[1] a brief consideration of the subject from this point of view, along with the results of experiments as to the effect of ethylene upon diastase and invertase with pure substrate material, was presented. No significant difference between the ethylene-treated and untreated materials was observed. The enzymes investigated were selected as representative of those concerned with normal ripening changes of carbohydrates and the original plan of experimentation anticipated studies upon other enzymes more definitely associated with color changes. It has been pointed out by Harvey[2] that an overdose of ethylene causes bananas to become brown. This coloration may be similar to leaf darkening and result from an increased hydrolysis of some glucoside followed by oxidase action upon the non-sugar component. It also seems probable that other coloration phenomena might have, as an initial stage, the change of a

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[1] Englis and Zannis, THIS JOURNAL, 52, 797 (1930).

[2] Harvey, Bulletin 247, U. of Minn., Agr. Exptl. Sta., October, 1928.

glucoside into its simpler constituents. Since emulsin, which is associated with hydrolysis of β-glucosides, has apparently not received attention in connection with ethylene treatments, a study of this enzyme was undertaken. Several factors influenced the selection of salicin as the substrate material. It can be obtained readily in a high state of purity. Its hydrolysis by the enzyme has been thoroughly studied by Hudson and Paine[3] and others[4] and the rate can be followed readily by both physical and chemical methods.

Experimental

Materials.—The emulsion was prepared from sweet almonds according to the directions of Morrow.[5] One portion of the emulsion was preserved in the dry state. Another portion was made into a 1% solution and preserved with toluene.

The salicin was obtained from the Pfanstiehl Chemical Company. Its melting point was 195–197° and the ash content 0.05%.

The ethylene was a commercial product supplied by the U. S. Industrial Alcohol Company.

Method.—The general procedure was the same as that employed in the earlier study of diastase. The substrate of salicin was buffered with an acetic acid–sodium acetate buffer at a PH of 4.66 before adding the enzyme. The progress of the hydrolysis was followed by polarimetric observations and by determination of the reducing sugar by the Munson and Walker method.

Experiment I

Procedure.—6.250 grams of salicin was dissolved in 200 cc. of buffer solution and the solution divided into two parts. One part was saturated with ethylene. Both portions were then warmed to 40° and 25 cc. of the fresh emulsin solution added to each. At various time intervals portions were withdrawn and sodium carbonate added to stop the action of the enzyme and hasten the establishment of the equilibrium value following mutarotation. The portions were then filtered and polarized in a 2-dm. tube.

TABLE I

EFFECT OF ETHYLENE UPON THE HYDROLYSIS OF SALICIN BY EMULSIN. PROGRESS OF REACTION FOLLOWED BY POLARIMETRIC METHOD

Salicin 2.5 g. per 100 cc.; temperature, 40°; PH 4.66

Experiment	Emulsin	Time, minutes	Rotation, 2-dm. tube Control, °V.	Ethylene treated, °V.
		0	−9.0	−9.0
		15	−7.1	−6.9
I	Fresh 0.2 g. per 100 cc.	30	−5.3	−5.0
		80	+0.4	−0.5
		1500	+4.0	+4.0
	Dry (after 30 days)	0	−8.9	−8.9
		15	−8.1	−8.2
II	0.2 g. per 100 cc.	30	−7.2	−7.1
		200	−1.4	−1.0

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[3] Hudson and Paine, THIS JOURNAL, 31, 1242 (1909).

[4] Kuhn and Sobotka, *Z. physik. Chem.*, **109**, 65 (1924).

[5] Morrow, "Biochemical Laboratory Methods," John Wiley and Sons, New York 1927, p. 286.

Experiment II

In a second experiment carried out thirty days later a 1% solution of the **dry emulsin** was prepared and the same procedure followed as in the first experiment. The results of the experiments are given in Table I.

Experiments III and IV were analogous to I and II except that the reaction was followed by determination of the reducing sugar produced. The quantities of materials used and results obtained are given in Table II.

TABLE II

EFFECT OF **ETHYLENE** UPON THE HYDROLYSIS OF **SALICIN** BY **EMULSIN**

Salicin, 1.25 g. per 100 cc.; temperature, 40°; PH 4.66

Experiment	Emulsin	Time, minutes	Cu$_2$O Control, g.	Cu$_2$O C$_2$H$_4$-treated, g.	Glucose Control, g.	Glucose C$_2$H$_4$-treated, g.	Hydrolysis Control, %	Hydrolysis C$_2$H$_4$-treated, %
		0	0.0065	0 0065	0 0027	0.0027	..	..
III	Presh0.2 g. per	4U	2783	2555	.1266	1 1 5	63	57
	100 cc	80	,3795	3664	.1777	1709	89	86
		0	0065	.0065	.0027	0027	..	..
IV	Dry after 30	15	.0361	.0300	.0152	.0126	6	5
	days 0.2 g.	30	0754	.0757	.0324	0324	16	16
	per 100 cc.							

Discussion

An examination of the tables shows practically no difference in the rate of hydrolysis in the salicin in the ethylene-treated samples and the controls in any of the experiments. The slight differences observed in favor of the controls are probably not significant. The emulsin on drying lost a great deal of its activity but the results with regard to ethylene were the same as with the fresh material.

In connection with the findings of this paper and the one preceding it[1] the results of a number of other studies of similar nature may be mentioned. Hirschfelder and Ceder[6] have carried out some very interesting experiments with ethylene attempting to extend the work upon fruits and vegetables to animals. Rats were given ethylene-treated drinking water and grown in atmospheres of varying concentrations of ethylene. The growth of the rats was not favorably affected. In supplementary work with enzymes they found that pepsin, trypsin and liver lipase were not activated by ethylene. However, they report that pancreatic amylase was activated. Johnson and Wormall[7] also report that potassium thiocyanate, a material which has been used to break the dormant period of potatoes and may be considered to fall in the same group of chemicals as ethylene, accelerated the first stages of hydrolysis of starch by saliva, malt and potato diastase but did not markedly increase the rate of formation of

[6] Hirschfelder and Ceder, *Am. J. Physiol.*, 91, 624 (1930).

[7] Johnson and Wormall, *Proc. Leeds Lit. Soc. Sci.*, Sec. 1, 318–324 (1928).

reducing sugars. Denny and associates,[8] who have been perhaps the most consistent contributors in this general field, have observed that under the conditions of their experiments sodium thiocyanate, thiourea and ethylene chlorohydrin all break the dormancy of potatoes. However, the increases in enzyme activity which were found from the treatment of the potatoes with chemicals were not direct effects of the chemicals on the enzymes but were indirect and brought about by the action of the chemical upon the tubers, since the treated juice of the potato failed to show significant differences from the control. This study relative to the treatment of the juice corresponds in principle to the method followed in this paper and the results obtained here are in agreement with its findings. Perhaps the apparent contradiction in the results obtained by Hirschfeld and Ceder[6] can be attributed to a lack of buffering or some other difference in experimental detail.

The results of these experiments suggest that a very complex system of reactions is taking place. The question might be raised as to whether or not studies as to the effect of ethylene or similar substances upon purified enzymes with pure substrate material should be abandoned. Perhaps mixtures of enzymes may be studied and some "key" reaction in the chain found. If not, one must come to the tentative conclusion of Denny that the chemicals seem to induce the living matter to produce larger amounts of (or more active) enzymes and their effect is not a direct one upon the enzymes.

Summary

The fact that ethylene hastens coloration of many fruits and vegetables gave rise to the belief that its effect might be associated with the activation of the enzyme responsible for the hydrolysis of many glucosides. For this reason a study was made of its influence upon the rate of hydrolysis of salicin by emulsin.

The rate of hydrolysis was followed by polarimetric observations and determinations of reducing sugar.

No acceleration of the reaction was observed in favor of the treated samples over the controls.

The results are in accord with the idea that ethylene does not directly affect the activity of enzymes, but acts indirectly through its effect upon the living matter.

URBANA, ILLINOIS

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[8] Denny, Miller and **Guthrie,** *Am. J. Bot.,* **17, 483 (1930).**

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF RRISTOL AND THE IMPERIAL COLLEGE OF TROPICAL AGRICULTURE]

THE CATECHIN OF THE CACAO BEAN

BY W. B. ADAM, F. HARDY AND M. NIERENSTEIN

RECEIVED NOVEMBER 20, 1930 PUBLISHED FEBRUARY 9, 1931

The presence of a catechin-like substance in the cacao bean was first definitely established by Ultée and van Dorssen,[1] although it appears fairly certain that previously to them Trojanowsky,[2] Hilger[3] and Schweizer,[4] seem to have observed such a substance in the cacao bean. Cacao-ole, the name adopted by Ultée and van Dorssen for the catechin, was shown by them to have the empirical formula $C_{16}H_{16}O_6$, to melt at 220° and to yield an acetyl derivative which melted at 153–154°. The empirical formula of Ultée and van Dorssen thus showed cacao-ole, $C_{16}H_{16}O_6$, to be a methyl derivative of catechin, $C_{15}H_{14}O_6$. The existence of such a methylated catechin in nature seemed to us of great interest, as so far no derivative of catechin has been recorded in the literature to be present in the plant. We have therefore investigated the West African cacao bean. The catechin thus obtained had the empirical formula $C_{15}H_{14}O_6$, melted at 229° and gave a pentaacetyl derivative melting at 151°. The same catechin was also obtained by us from the cacao bean grown in Trinidad. Since both catechins thus derived from Forostero beans,[5] and Ultée and van Dorssen had obtained their cacao-ole from the cacao bean grown in Java, which belongs to the Criollo class, we also investigated the catechin present in the Java cacao bean. Here again a catechin having the empirical formula $C_{15}H_{14}O_6$ was obtained, and a direct comparison of the three catechins proved them to be identical in every respect. In view of this we wrote to Dr. Ultée, who kindly sent us some of his original cacao-ole. On purification, the latter proved also to have the empirical formula $C_{15}H_{14}O_6$, to melt at 229° and to yield a pentaacetyl derivative which melted at 151°. We thus find that the catechin present in the cacao bean is not a methyl derivative of catechin but catechin itself, namely, *l*-acacatechin, one of the catechins present in the cutch-producing acacias,[6] as evident from a direct comparison between the catechin from the cacao bean and I-acacatechin. Thus cacao catechin and *l*-acacatechin melt at 229" and rotate in aqueous solution $[\alpha]_D\ -69°$; they both give penta-

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[1] Ultée and van Dorssen, "Bijdrage tot de kennis der op Java gecultiveerde Cacaosoorten," reprint no. 33, 2d series of Mededeelingen van het Algemeen-proefstation op Java te Salatiga. 1909.

[2] Trojanowsky, "Beiträge zur pharm. u. chem. Kenntnis des Cacao," Dorpat, 1875.

[3] Hilger, *Apoth.-Ztg.*, 7, 469 (1892).

[4] Schweizer, *Pharm.* Ztg., 43, *380* (1898).

[5] Although the Trinidad cacao bean is supposed to be derived from Criollo stock, it has more characteristics of the Forostero than of the Criollo.

[6] Nierenstein, *J. Indian Chem. Soc.*, 7,279 *(1930).*

acetyl derivatives which melt at 151° and rotate $[\alpha]_D$ $-12°$ in tetrachloroethane. Furthermore, neither the catechins themselves nor their acetyl derivatives, respectively, show depression in their melting points on admixture.

The importance of catechin in the production of the red and brown coloring matters and the tannins of the cacao bean have been dealt with in a previous communication, which describes a quantitative method for the estimation of catechin in the cacao bean. From the results with cacao beans from West Africa, Java, Guayaquil, Trinidad, Costa Rica and Bahia it is evident that the catechin content of the cacao bean is about 0.8%.[7]

Experimental

The beans used in the investigation were freshly collected, immersed in boiling water so as to destroy enzymes and sun dried. After removal of the shells, the raw nibs were ground in a mechanical mortar and exhaustively extracted in a large Soxhlet apparatus with petroleum ether. The material was then removed from the extraction apparatus, re-ground, mixed with acid-treated white sand and again extracted for several days with petroleum ether. The product was then freed from petroleum ether by exposure to air, powdered and extracted for a week with chloroform. This treatment was found to be necessary in order to remove completely the last traces of fat and the xanthine bases. No trace of catechin was found in the petroleum ether and chloroform extracts. The dried product was then treated as before and exhaustively extracted for several weeks with ether. The solid left on evaporation was practically pure *l*-acacatechin. It was obtained in colorless, anhydrous needles by purification with lead acetate, and crystallization from water slightly acidulated with acetic acid.[8] This process of purification was also found necessary in the case of Dr. Ultke's specimen. The acetylation was carried out by heating with acetic anhydride. The acetyl derivative crystallized in beautiful thick needles from alcohol, a few drops of acetone being added. The following table summarizes the analytical data obtained for the products dried at **160°** (catechin) and **110°** (pentaacetyl derivative), respectively.

TABLE I

ANALYTICAL DATA

	Catechin, calcd. for $C_{15}H_{14}O_6$: C, 62.06; H, 4.82 Found, %		**Pentaacetyl derivative, calcd. for $C_{15}H_9O_6[CO.CH_3]_5$: C, 60.02; H, 4.82 Found, %**	
Source of cacao bean	C	H	C	H
West-Africa [Accra]	61.92, 62.13	5.07, 5.15	59.72, 60.01	4.97, 4.89
Java	61.97, 62.00	4.99, 5.12	60.03, 59.83	5.03.4.93
Trinidad .	62.09, 61.84	5.02, 4.87	59.76, 59.89	5.12, 5.19
Java [Dr. Ultée's specimen]	61.87, 61.92	5.09, 5.11	59.83	5.02

Summary

It is shown that the catechin of the cacao bean is identical with one of the three catechins present in the heartwood of the cutch-producing acacias, namely, *l*-acacatechin.

BRISTOL, ENGLAND

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[7] Adam, *Analyst,* 53, **369 (1928)**

[8] Nierenstein, J. *Chem. Soc.,* **121,608 (1922).**

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OR CHEMISTRY AND SOILS]

TEPHROSIN. I. THE COMPOSITION OF TEPMROSIN AND ITS RELATION TO DEGUELIN

BY E. P. CLARK

RECEIVED NOVEMBER 20, 1930 PUBLISHED FEBRUARY 9, 1931

Hanriot isolated from the leaves of ***Cracca*** *(Tephrosia) vogelii* a substance which he named tephrosin.[1] To this material he assigned the formula $C_{31}H_{26}O_{10}$ and reported its melting point as 187°. His results were later confirmed by work published in the Bulletin of the Imperial Institute for 1915[2] except that the melting point of tephrosin was given as 192°.

In the studies in progress in this Laboratory upon the constituents of certain tropical fish-poisoning plants, an examination of the leaves of ***Cracca*** *vogelii* from Africa and Sumatra resulted in the isolation of a physiologically active crystalline material corresponding to that obtained by Hanriot. The preparation was a mixture of at least two compounds which were carefully separated and characterized. One was deguelin, m. p. 171°,[3] and the other was a colorless crystalline substance with a melting point of 197–198°.

At the time these experiments were being carried on, the same compounds, together with several others, were also found in the rotenone mother liquors from derris and cub6 roots.[4] When working with these materials difficulty in separating the individual constituents by fractional crystallization was experienced, due to the similarity of the solubilities of the several compounds in many solvents. However, as the separation proceeded, a fraction with a melting point of 180–185° was invariably obtained. It was unusually hard to resolve, but optical methods showed it to be essentially deguelin and the compound melting at 198°. This preparation was similar to the one obtained by the writer from ***Cracca*** *vogelii* and it appears likely that it was such a mixture that Hanriot described as tephrosin. Since a mixture of these two substances melting at 187° would contain more of the compound melting at 19S° than deguelin, the name tephrosin should be assigned to the former substance. In this and subsequent communications upon the subject this name will be adopted.

To obtain tephrosin, and the substances with which it is associated, it is necessary to treat the plant extractives in which it is found with an alkali.[4] A mixture is thus obtained from which tephrosin may be separated by fractional crystallization, but since purification in this way is un-

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[1] Hanriot, *Compt. rend.*, *144*, *150 (1907); Compt rend. soc. biol.*, *62*,*384 (1907)*.

[2] *Anon., Bull. Imp. Inst.*, **13**, 61 *(1915)*.

[3] Clark, *Science*, *71*, 396 (1930).

[4] Clark, THIS JOURNAL, **53**, 313 *(1931)*.

usually difficult, it is expedient, after several fractionations, to destroy the contaminating materials (mostly deguelin) by selective oxidation. In the experimental part directions are given for conducting such a procedure.

Tephrosin, prepared by either method, crystallizes in colorless prisms whose melting point is 198° (corr.), but this value varies somewhat depending upon the rate of heating. The substance has the molecular formula $C_{23}H_{22}O_7$ and contains two methoxyl groups.

When tephrosin is dissolved in a mixture of one volume of concentrated sulfuric acid and two volumes of acetic acid and the solution maintained at about 60° for fifteen minutes, tephrosin loses a molecule of water, forming dehydrodeguelin.[4] The same result is also obtained when tephrosin is boiled with a mixture of acetic anhydride and sodium acetate. The reactions show that tephrosin is intimately related to deguelin and possibly is a hydroxydeguelin. As yet direct evidence for an hydroxyl group in tephrosin has not been obtained, but in certain derivatives of this group of compounds an hydroxyl group may be present that gives extremely poor yields or fails entirely to form acyl or alkyl derivatives. Since dehydrodeguelin is a lactone it follows that tephrosin is a lactone also.

Another reaction presented as confirmatory evidence of the C_{23} formula for tephrosin is its behavior toward potassium permanganate. When oxidized with this reagent in an acetone solution, tephrosin yields a dicarboxylic acid, $C_{23}H_{22}O_{11}$, which melts at 221°. This acid has been designated as tephrosindicarboxylic acid.

Experimental

Tephrosin from Cracca Vogelii.—Two and four-tenths kg. of the ground leaves of *Cracca vogelii* were percolated with ether and the extract was concentrated to a thick sirup. When this sirup was dissolved in 400 cc. of hot alcohol and allowed to cool, 1 g. of fine colorless waxy crystals separated. (Since this material was not of immediate interest it was not investigated.) One hundred cc. of the alcoholic filtrate from the waxy crystals, representing 600 g. of leaves, was dissolved in 750 cc of boiling alcohol; 750 cc. of hot water was added, and the resulting turbid liquid was filtered through norit. The filtrate was concentrated under reduced pressure until the extractives separated as a gummy material which adhered to the flask. The residual liquid was decanted, and the flask was dried with a current of air. The gummy material was dissolved in 100 cc. of boiling methanol and treated with 0.5 g. of dry sodium carbonate. Crystallization began at once and was completed after several hours. The yield was 2 g. or 0.33%.

The crude crystalline material was dissolved in boiling alcohol, filtered through norit and allowed to crystallize. The compound which separated was identified as deguelin by its melting point (171°), mixed melting point and optical properties. The deguelin mother liquors were concentrated to one-fourth their volume and allowed to crystallize. A small quantity of colorless prisms, m. p. 188–191°, was obtained. This substance was dissolved in a small quantity of hot chloroform and about 20 volumes of methanol added. The resulting solution was evaporated to one-half its volume and set aside to crystallize. This procedure was repeated until the product had a constant melting point of 197–198°.

The tephrosin thus obtained consists of stout six-sided colorless prisms. The extinction is inclined and the elongation is negative. In convergent polarized light with crossed nicols, partial biaxial figures are common. The optic axis of fragments is usually inclined. The refractive indices are: η_α, 1.590 (common); η_β, indeterminate, $\eta_\gamma > 1.74$. An intermediate index, η_ι, 1.680 is also common.[5]

Anal. Calcd. for $C_{23}H_{22}O_7$: C, 67.30; H, 5.41; OCH_3 (2), 15.1. Found: C, 67.31; H, 5.47; OCH_3, 15.2.

Tephrosin from Derris and Cubé Roots.—In the recent article upon deguelin[4] details were given concerning the methods for obtaining a crystalline mixture from the rotenone mother liquors of derris and cubé roots. Since tephrosin is so intimately associated with deguelin in these mixtures, details for preparing a crude tephrosin was of necessity included in the preparation of deguelin. The fraction (m. p. 180–185°) which contained the most tephrosin was subjected to fractional crystallization until a product having a melting point of 198° was obtained. This was analytically and optically identical with tephrosin from *Cracca* leaves.

A more convenient method of preparing pure tephrosin is to destroy the deguelin in the mixture melting at 180–185° with chromic acid. This may be done as follows: 25 g. of the crude mixture (m. p. 180–185°) is dissolved in 500 cc. of boiling acetic acid. To this solution is added 40 cc. of a 10% acetic acid solution of crystalline sodium dichromate, and after the mixture has been allowed to react for five minutes, 500 cc. of boiling water is added. The turbid liquid is immediately filtered through norit and allowed to crystallize. Usually 12 g. of tephrosin with a melting point of 192–193° is obtained. When this product is recrystallized two or three times from 95% alcohol, it has a melting point of 197–198° Tephrosin prepared in this manner has the same optical properties as the specimens obtained by fractional crystallization

Anal. C, 67.32; H, 5.36; OCH_3, 15.6.

The Action of Sulfuric **and** Acetic Acids upon **Tephrosin.—One** gram of tephrosin was warmed to about 60° for fifteen minutes with a solution of 3 cc. of concentrated sulfuric acid in 6 cc. of acetic acid. Fifty cc. of water was then added to the mixture and the precipitate formed was removed and washed with water until it was free from sulfuric acid. The product was dried and dissolved in a small volume of hot chloroform, filtered through norit and five volumes of methanol added to the filtrate. Crystallization began at once, yielding 0.8 g. of pure dehydrodeguelin. The product was identified by its melting point, 233°. When it was mixed with dehydrodeguelin from deguelin, no melting point depression occurred. It also possessed the optical properties characteristic of dehydrodeguelin.

Action of Acetic Anhydride upon Tephrosin.—A mixture of 0.5 g. of tephrosin, 0.25 g. of potassium acetate and 4 cc. of acetic anhydride was boiled for ten minutes. The condenser was then disconnected, and about two-thirds of the anhydride was removed by distillation. The remaining anhydride was carefully decomposed with methanol, after which ten volumes more of methanol were added Crystallization began at once, yielding a product which melted at 228–230°. Upon recrystallization from chloroform and methanol it melted at 233°, and when it was mixed with dehydrodeguelin no depression of the melting point occurred. Its optical properties were the same as those of dehydrodeguelin.

Tephrosindicarboxylic Acid.—A constantly stirred solution of 5 g. of tephrosin in 300 cc. of acetone, maintained at a temperature between 15 and 20°, was treated with

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[5] The optical data recorded in this paper were determined by George L. Keenan of the Food and Drug Administration, U. S. Department of Agriculture. Appreciation is expressed for this cooperation.

10 g. of potassium permanganate until the color due to the permanganate ions disappeared. The resulting manganese dioxide was removed by filtration, washed with acetone and then digested for two hours with 500 cc. of boiling absolute alcohol. The hot alcoholic extract was filtered, concentrated to 40 cc. and allowed to crystallize.

The resulting potassium salt, which weighed 1.5 g., was then dissolved in 100 cc. of water and the solution filtered through norit. The filtrate was heated to boiling, and dilute sulfuric acid was added until an acid reaction to Congo red was obtained. Upon standing overnight the liquid deposited 1.4 g. of rod-like plates, which melted at 220° with decomposition.

The acid was recrystallized from 1.5% boiling aqueous solution, from which it separated as clear-cut tabular crystals and rods which melted at 221° with decomposition (corr.). The substance has inclined extinction, positive elongation and the following indices of refraction: n_α, 1.530; n_β, indeterminate, and n_γ, 1.640; both ±0.003.

Anal. Calcd. for $C_{23}H_{22}O_{11}$: mol. wt. 474.3; OCH_3 (2), 13.1; C, 58.21; H, 4.68. Found: acid equivalent (2 COOH), 472; OCH_3, 13.1; C, 58.37; H, 4.73.

Summary

1. Deguelin, m. p. 171°, and a compound melting at 198°, were isolated from the leaves of *Cracca vogelii*, derris root and the roots of *Lonchocarpus nicou* (Cubé root).

2. These two substances form a mixture which is difficult to separate by fractional crystallization and which appears to be the material designated by Hanriot as *tephrosin*.

3. It is proposed that the name tephrosin should be retained for the compound with the melting point of 198°.

4. Tephrosin is a dimethoxy lactone, $C_{23}H_{22}O_7$, which, under the influence of certain dehydrating agents, loses one molcule of water, forming dehydrodeguelin.

5. It is suggested that tephrosin is a hydroxydeguelin.

6. The action of potassium permanganate upon tephrosin results in the formation of a dicarboxylic acid, $C_{23}H_{22}O_{11}$.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE.
XI. THE RELATION BETWEEN ISOROTENONE AND ROTENONE

BY H. L. HALLER

RECEIVED NOVEMBER 20, 1930 PUBLISHED FEBRUARY 9, 1931

Rotenone on catalytic hydrogenation with one mole of hydrogen yields a mixture of dihydrorotenone and rotenonic acid.[1] Rotenonic acid on hydrogenation is reduced to dihydrorotenonic acid, which can also be obtained by the hydrogenation of dihydrorotenone.[1]

Isorotenone,[2] an isomer of rotenone, is obtained by dissolving rotenone in a solution of glacial acetic acid and concentrated sulfuric acid and then adding the resulting cherry red solution to water. In its chemical behavior isorotenone exhibits most of the typical reactions of rotenone. It yields a dehydro derivative, a diketone, isoderritol and isotubaic acid. The only marked difference is in its behavior on catalytic hydrogenation. Whereas rotenone is readily reduced with catalytic hydrogen to an acid, and a dihydro derivative, isorotenone is reduced only with great difficulty and so far it has not been possible to obtain from it an acid corresponding to rotenonic acid.

Isoderritol and isorotenol are not reduced to acids under the conditions employed for the reduction of derritol and rotenol.

Tubaic acid,[3] which is obtained on boiling an alcoholic potassium hydroxide solution of rotenone, is readily reduced to a dihydro derivative.

Isotubaic acid[4] (rotenic acid), which is obtained on isomerization of tubaic acid, is not easily hydrogenated but can be reduced under certain conditions, as has been shown by Butenandt and Hildebrandt[5] and by Takei, Koide and Miyajima.[6]

Tubaic acid is optically active, whereas isotubaic acid is optically inactive. Dihydroisotubaic acid is a racemic mixture. It has been resolved[5,6] into its enantiomorphs and the levo form has been found to be identical with dihydrotubaic acid. Thus it is definitely established that the isomerization of tubaic acid into isotubaic acid is due to the migration of a double bond.

The facts that isorotenone yields isotubaic acid under the same conditions that rotenone yields tubaic acid and that tubaic acid can be isomerized

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[1] F. B. LaForge and L. E. Smith, THIS JOURNAL, 51,2574 (1929).

[2] S. Takei, *Biochem.* Z., 157, 1 (1925); *Ber.*, 61, 1003 (1928).

[3] T. Kariyone, Y. Kimura and K. Kondo, J. *Pharm. Soc.* (Japan), 514, 1094 (1924); ibid., 518,377 (1925); S. Takei, Ber., 61, 1003 (1928).

[4] S. Takei, *Biochem. Z.*, 157, 1 (1925); A. Butenandt and F. Hildebrandt, Ann., 477,245 (1930); H. L. Haller and F. B. LaForge, THIS JOURNAL, 52,3207 (1930).

[5] A. Butenandt and F. Hildebrandt, Ann., 477,245 (1930).

[6] S. Takei, M. Koide and S. Miyajima, *Ber.*, 63, 1369 (1930).

to isotubaic acid, lead to the conclusion that the same groupings are involved in the isomerization of rotenone into isorotenone as in the transformation of tubaic acid into isotubaic acid.

On oxidation with permanganate, tubaic acid yields acetic acid, whereas isotubaic and dihydrotubaic acid give isobutyric acid.[7] Takei and Koide[8] have obtained a methyl ketone on ozonization of tubaic acid. The presence of an isoallyl group in tubaic acid and in rotenone is therefore definitely established; isotubaic acid, dihydrotubaic acid and isorotenone, on the other hand, contain the isopropyl group.

As it has been shown that the double bond in tubaic acid which is readily reduced is in the isoallyl group and that isotubaic acid does not reduce readily, it appears fairly well established that the double bond from the isopropylene group in tubaic acid is the one which migrates on isomerization.

The fact that rotenone readily yields an acid on catalytic hydrogenation, whereas isorotenone does not, indicates that there is a close relation between the lactone ring and the migratory double bond, and that the cleavage of the lactone ring by hydrogenation depends upon the position of the unsaturated bond. It has not yet been possible to fix the position of the lactone ring, but in a recent paper it has been shown that acid derivatives obtained by hydrogenation of rotenone do not yield tubaic acid, but that the hydroxyl group resulting from the hydrolytic opening of the lactone ring is necessary for its formation.[9]

In an attempt to isomerize rotenonic acid to isorotenonic acid with glacial acetic and sulfuric acids, a product insoluble in alkali was obtained. It is not a mixed anhydride since it was recovered unchanged on refluxing in methyl alcohol solution, but is isomeric with rotenonic acid and dihydrorotenone. It will be called β-dihydrorotenone. It is probably a saturated lactone formed by the migration of a double bond with subsequent ring closure. As is well known, unsaturated acids can be transformed into saturated lactones by means of acid.

The formation of β-dihydrorotenone is further evidence that there is a close association between the lactone ring and the migratory double bond.

Jacobs and Scott[10] have recently shown that γ- and 6-lactones which contain a double bond in the β, y- or γ,δ-position readily yield desoxy acids on catalytic hydrogenation. When the double bond is in the α,β-position the ring is not opened but, instead, saturated lactones are obtained.

It is possible that when rotenone is isomerized to isorotenone, the double bond from the isopropylene group migrates to an α,β-position to the lactone

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[7] S. Takei and M. Koide, *Bull. Inst. Phys. Chem. Res.*, *8*, *64* (1929); *Ber.*, 62, 3030 (1929); Takei and Miyajima, *Bull. Inst. Phys. Chem. Res.*, *8*, 61 (1929).

[8] S. Takei and M. Koide, *Ber.*, 62, 3030 (1929).

[9] H. L. Haller and F. B. LaForge, THIS JOURNAL, 52,4505 (1930).

[10] W. A. Jacobs and A. B. Scott, *J. Biol. Chem.*, 87,601 (1930).

group and that the double bond becomes part of a conjugated system, which rearrangement might explain why isorotenone does not yield an acid on hydrogenation and why it is reduced only with difficulty.

The isomerization of rotenonic acid to a saturated lactone may be explained by rearrangement, accompanied by the disappearance of the double bond. No such change is possible in the case of dihydrorotenonic acid because the double bond in the isoallyl group has been reduced.

β-Dihydrorotenone is optically active. In alcohol solution it reduces Fehling's solution. It is not reduced with platinum oxide and hydrogen in ethyl acetate solution. On refluxing in alcoholic potash solution, an acid isomeric with dihydrotubaic acid is obtained. The same acid is obtained on fusion with potassium hydroxide. Like rotenone, β-dihydrorotenone yields a yellow dehydro compound on mild oxidation, and with stronger oxidizing agents, a diketone. Dehydro-β-dihydrorotenone on boiling with alcoholic potash and zinc adds two moles of water to form an acid corresponding to dihydro-dehydrodihydroxyrotenonic acid (dihydroderris saure, Butenandt) which has been termed dehydrodihyroxy-β-dihydrorotenonic acid. This acid also yields derric acid on oxidation with hydrogen peroxide in alkaline solution.

Experimental

β-Dihydrorotenone.—Five grams of rotenonic acid was dissolved with gentle heating in a solution of 16.5 cc. of concentrated sulfuric acid and 60 cc. of acetic acid. The cherry red solution was slowly poured into 500 cc. of water with constant stirring. The precipitate was filtered off, washed with water and dissolved in ether. The ether solution was washed with 5% potassium hydroxide, then with water and then dried over sodium sulfate. The substance readily crystallized after most of the ether was distilled off. It melted at 156". In alcohol solution it reduced Fehling's solution; in chloroform, $[\alpha]^{34}_{D}$ −26.5° (C = 5.86).

Anal. Subs., 0.0790, 0.0782, 0.0987: CO_2, 0.2000, 0.1984, 0.2522; H_2O, 0.0432, 0.0416, 0.0531. Subs., 0.0220, 0.0214; AgI, 0 0268, 0.0261. Calcd. for $C_{23}H_{24}O_6$: C, 69.69; H, 6.06, $2OCH_3$, 15.65. Found: C, 69.08, 69.20, 69.68; H, 6.08, 5.92, 5.96; OCH_3, 16.08, 16.09.

One gram of β-dihydrorotenone was dissolved in 50 cc. of methyl alcohol, and the solution was refluxed for three hours. It was then concentrated to about half its volume and cooled. The substance which readily crystallized proved to be unchanged β-dihydrorotenone. The melting point was 156°. β-Dihydrorotenone in ethyl acetate solution with platinum oxide catalyst absorbed no hydrogen.

β-Dihydrotubaic Acid.—Five grams of β-dihydrorotenone was dissolved in a solution of 5 g. of potassium hydroxide in 50 cc. of alcohol and 5 cc. of water. The solution was refluxed for three hours and then poured into 500 cc. of water. The acid was isolated by the procedure described for the preparation of tubaic acid.[11] It melted at 175–176° with decomposition. In alcohol it gave a purple color with ferric chloride. It contained no methoxyl.

Anal. Subs., 0.0844, 0.0827: CO_2, 0.2002, 0.1946; H_2O, 0.0467, 0.0469. Calcd.

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[11] H. L. Haller and F. B. LaForge, THIS JOURNAL, 52,3207 (1930).

for $C_{12}H_{14}O_4$: C, 64.86; H, 6.31. Found: C, 64.70, 64.16; H, 6.15, 6.31. 0.0245 g. of subs. required 1.10 cc. of N/10 KOH; 0.242 g. of subs. required 1.10 cc. of N/10 KOH. Calcd. mol. wt., 222. Found: 223,220.

Alkali Fusion of β-Dihydrorotenone.—Two grams of β-dihydrorotenone was intimately mixed with 18 g. of powdered potassium hydroxide and 1 cc. of water in a nickel crucible. The reaction mixture was heated with constant stirring in a metal-bath at 225° for twenty-five minutes. After cooling, the fusion mass was dissolved in water and the acid isolated by the procedure previously described.[10] The acid proved to be identical with the acid obtained by the action of alcoholic potash on β-dihydrorotenone.

β-Dihydrorotenone.—Four grams of β-dihydrorotenone was dissolved in 120 cc. of glacial acetic acid, and the solution was heated to boiling under a reflux condenser. During the course of three hours, 8 g. of chromium trioxide in 200 cc. of glacial acetic acid was added. The solution was then concentrated to half its volume. On cooling fine yellow needles crystallized out which decomposed at about 310°.

Anal. Subs., 0.0808, 0.0804: CO_2, 0.1982, 0.2001; H_2O, 0.0351, 0.0349. Subs., 0.0223, 0.0223: AgI, 0.0247, 0.0248. Calcd. for $C_{23}H_{20}O_7$: C, 67.61; H, 4.93; $2OCH_3$, 15.20. Found: C, 66.90, 67.88; H, 4.83, 4.82; OCH_3, 14.62, 1468.

From the mother liquors obtained in the oxidation described above a minute quantity of acid was isolated which was found to be identical with the acid obtained by the action of alcoholic potash on β-dihydrorotenone.

Dehydro-β-dihydrorotenone.—One gram of β-dihydrorotenone was dissolved in 50 cc. of boiling 95% alcohol. A solution of 1.8 g. of potassium fenicyanide and 0.27 g. of potassium hydroxide in 15 cc. of water was added to the boiling solution. The reaction mixture was allowed to stand overnight. Water was then added and the resulting crystalline precipitate was filtered off, washed with water and then with alcohol. It melted at 269°.

Anal. Subs., 0.0823, 0.0884: CO_2, 0.2100, 0.2250; H_2O, 0.0419, 0.0441. Calcd. for $C_{23}H_{22}O_6$: C, 70.00; H, 5.58. Found: C, 69.62, 69.47; H, 5.70, 5.58.

β-Dihydrorotenolone.—One gram of β-dihydrorotenone was dissolved in a solution of 2.5 g. of potassium acetate in 50 cc. of absolute alcohol. To the hot solution 0.8 g. of iodine dissolved in 50 cc. of absolute alcohol was slowly added. On cooling, a cream-colored product crystallized. It was recrystallized from chloroform–ethyl alcohol. It melted at 274". The compound was an hydroxy derivative of β-dihydrorotenone.

Anal. Subs., 0.0855, 0.1009: CO_2, 0.2109, 0.2495; H_2O, 0.0441, 0.0511. Subs., 0.0212, 0.0219: AgI, 0.0248, 0.0255. Calcd. for $C_{23}H_{24}O_7$: C, 67.00; H, 5.82; $2OCH_3$, 15.05. Found: C, 67.27, 67.44; H, 5.73, 5.63; OCH_3, 15.45, 15.37.

On boiling with alcoholic sulfuric acid, β-dihydrorotenolone yielded a yellow compound which was identical with the dehydro compound obtained by oxidation of β-dihydrorotenone with potassium ferricyanide.

The filtrate from the β-dihydrorotenolone was concentrated to dryness and water was added. The undissolved substance was filtered off, dried and recrystallized from 95% alcohol. It melted at 224°. Analysis indicated it to be the acetyl derivative of the hydroxy compound obtained above.

Anal. Subs., 0.0945, 0.0907: CO_2, 0.2288, 0.2195; H_2O, 0.0473, 0.0464. Calcd. for $C_{25}H_{26}O_8$: C, 66.08; H, 5.75. Found: C, 66.03, 66.00; H, 5.56, 5.68.

Dehydrodihydroxy-β-dihydrorotenonic Acid.—Eight-tenths gram of dehydro-β-dihydrorotenone was refluxed with 5 cc. of 40% potassium hydroxide, 20 cc. of ethyl alcohol and 2 g. of zinc dust for one and one-half hours. The zinc was removed by filtration and the solution was acidified with dilute sulfuric acid. After adding water to the solution it was cooled and extracted with ether. The ether extract was washed with water and dried over sodium sulfate. The ether was removed and the substance was crystallized from butyl ether. It melted at 149°.

Anal. Subs., 0.0927: CO_2, 0.2177; H_2O, 0.0506. Calcd. for $C_{23}H_{26}O_8$: C, 64.16; H, 6.09. Found: C, 64.05; H, 6.11.

Oxidation of **Dehydrodihydroxy-β-Dihydrorotenonic Acid** to Derric Acid.—One gram of acid was dissolved in 12 cc. of 5% sodium hydroxide solution. The solution was gently heated and 3 cc. of 30% hydrogen peroxide was gradually added. The solution was finally heated to boiling for a few minutes, then cooled and acidified with dilute sulfuric acid. The solution was extracted with ether, the ether extract was washed with water and dried over sodium sulfate. After removal of the ether the substance was crystallized from butyl ether. It melted at 167° and was found to be identical with derric acid.

Summary

Rotenonic acid in glacial acetic acid and sulfuric acid is isomerized to a substance which is insoluble in alkali and appears to be a saturated lactone. This compound has been named β-dihydrorotenone.

β-Dihydrorotenone gives the typical reactions of rotenone. It yields a dehydro compound which adds two moles of water to form an acid. It gives a diketone. With potassium hydroxide it yields an acid isomeric with dihydrotubaic acid.

A possible explanation is given of the fact that rotenone is readily reduced and isorotenone is not, and a relation between the two is indicated.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

THE SPECTROCHEMISTRY OF FURAN AND ITS DERIVATIVES[1]

BY EVERETT C. HUGHES AND JOHN R. JOHNSON

RECEIVED NOVEMBER 21, 1930 PUBLISHED FEBRUARY 9, 1931

Absorption spectra and molecular refraction have proved to be of considerable value in attacking chemical problems from a physical standpoint. In the furan series no extensive study has been made of these optical properties, although a number of observations are reported in the literature. The present work was undertaken with the object of making a rather extensive study of furan derivatives with the idea of discovering any general relationships which might prove useful in elucidating the structure and behavior of furan and its derivatives.

Preliminary observations of absorption spectra showed that furan and its simpler derivatives do not exhibit selective absorption in the visible and ultraviolet regions (to 2200 Å.). It was hoped that there would be a difference in the absorption spectra of the isomeric alpha- and beta-sub-

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[1] This article is an abstract of a thesis submitted to the Faculty of the Graduate School of Cornell University by Everett C. Hughes, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1930.

stituted furans that would be of value in distinguishing between them. Even in the case of the carboxylic acid derivatives, which do exhibit a characteristic absorption, there was not observed any regular or sufficient difference that would be of value in distinguishing between isomeric compounds. The only real difference lies in the molecular absorption coefficients (Fig. 2), which are consistently higher for the alpha-derivatives than for the beta-derivatives. These differences are directly related to the differences in optical dispersion; the latter, as will be shown below, prove to be of value as a criterion for distinguishing between the alpha- and beta-substituted derivatives.

Early investigations of the refractive index of compounds containing the furan ring have shown that the law of refraction equivalence is not strictly followed.[2] From theoretical considerations of molecular refraction as presented by Lorentz and discussed by later investigators[3] it appears that no absolute agreement between the calculated and observed values can be expected.

It was found, however, that the furan derivatives under examination could be divided into two categories on the basis of the differences between the observed and calculated values. Furthermore, the exaltations of the dispersion of compounds of the furan series may furnish information bearing upon the fundamental question of the structure of the ring and the position of substituents.

In order to provide data for study, furan and twenty furan derivatives were prepared in a high state of purity, and their refractive indices and densities were determined. These data, together with a number of values taken from the literature, are shown in Table V. The calculations made from these observations are collected in Table I.

An examination of the results indicates that these furan derivatives can be divided into two categories: one in which the value EMR is negative, and another in which this value is positive.

In the first class are found furan and all of the derivatives (Table I, 1–13) in which the substituents do not contain a double bond on the atom immediately attached to the ring in the alpha-position.[4] These compounds

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[2] (a) Brühl, *Ann.*, 235, 1 (1886); (b) Nasini and Carrara, *Gazz. chim. ital.*, **24**, I, 255 (1894); (c) Auwers, *Ber.*, 45, 3077 (1912).

[3] (a) Lorentz, "The Theory of Electrons," B. G. Teubner, Leipzig, 1909, p. 89; (b) Swietoslawski, THIS JOURNAL, 42, 1945 (1920); (c) Fajans and Knorr, *Ber.*, 59, 249 (1926).

[4] Ethyl pyrotritarate (2,5-dimethyl-3-carbethoxyfuran) is an exception to this statement. If the above constitution is correct, there is present a cross-conjugated system, the effect of which is uncertain—due to the lack of a sufficient number of known examples for examination. The only other available example of cross-conjugation is **2-methyl-3-carbethoxyfuran,** which is not an exception to the general statement given

TABLE I

REFRACTOMETRIC DATA FOR DERIVATIVES OF FURAN

No.	Compound	MR_D obs.	EMR_D[a]	$E_{\Sigma\beta-\alpha}$[b]	$E_{\Sigma\gamma-\alpha}$	EMR_∞	Constants of Sellmeir equation		
							M	λ_0	$C+1$
1	**Furan**	18 426	−0 761	−11 57	−6 11	−0 612	143407	1572	1 9762
2	2-Methylfuran	23 337	− 462	13 0	10 0	− 474	1 77000	742	2 00105
3	**2,5-Dimethylfuran**[c]	28 178	− 239	3.88	4 5	− 267	1 75185	334	2 03167
4	**Furfuryl** alcohol	24 874	− 450	0.0	1 0	− 410	1 74927	1478	2 15834
5	**Furfuryl** acetate	33.920	− 769	3 93	5 36	− 669	1 47193	1575	2 08682
6	Ethyl furylpropionate	43 474	− 451		5 50	− 008	0 80218	2791	2 09081
7	Furylbutanone	37 530	− 134	2 84	7 86	− .209	1 86697	202	2 10587
8	Furylpentanone	42 083	− 199	0 0	9 78	− .235	1 70486	912	2 10115
9	2-Chlorofuran	23 420	− 628	− 3 77	1 2 4	− 517	163804	1553	2 07304
10	3-Chlorofuran	23 157	− 891	−9 62	−9 49	− .745	1 58428	1460	2 07993
11	2-Bromofuran	26 119	− 825	4 0	1 0	− 947	2 32088	796	2 17583
12	3-Bromofuran	28 868	−1 078	−13 5	−12 4	− .996	1 80747	1581	2.18264
13	**2-Methyl-3-** carbethoxyfuran	38 267	−1 04	−8 25	−12 08	− 757	1 1147	100	1 9725
14	Ethyl furoate	35 61	0 921	43 0	47 8	0 615	1 98841	1712	2 09814
15	Ethyl 5-chlorofuroate	40 94	1 384	54 2	60 9	1 051	2 03544	2006	2 16719
16	**Ethyl** 3 chlorofuroate	40 37	0 814	40 1	47 5	0 55	1 76727	1972	2 15016
17	Methyl **furoate**[e]	30 896	825	42 0	44 5	511	2 30746	1393	2 1343
18	Propyl **furoate**[g]	40 255	948	38 9	41 0	.572	2 12725	1183	2 10839
19	Ethyl pyrotritaratef	44 618	693		20 1	529	1 7509	1196	2 10418
20	**Furyl** cyanide	24 40	89	33 2	48 3	667	194803	2130	2 12493
21	**Furfural**[d]	25 42	1 61	95	110	1040	3 25164	2042	2.22256
22	Furylethylene	29 58	1 63	60 2	79 4	1 257	2 54077	2325	2 15765
23	Furylbutenone	42 72	5 523	340 6	421	2 868	4 37428	2967	2 32375
24	Furylpentenone	46 634	4 824	301	376	2 921	4 08374	2888	2 336
25	Ethyl furylacrylate	48 27	4.481	161 0	227 1	3 203	3 4039	2754	2 26431
26	**Furfural pinacolone**	56 57	5.524	201.8	268.5	3.55	3.30667	2983	2.27162

[a] $EMR_D = MR_D$ observed − MR_D calculated. The revised values of Eisenlohr were used for the atomic refractions [Landolt-Bornstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 5th Ed., Vol. II, 1923, p. 985]. The furan ring was considered to have two ethylenic double bonds and an ethereal oxygen atom.

[b] $E_{\Sigma\beta-\alpha}$ is calculated from the specific refractions according to the empirical formula of Auwers (see below).

[c] **Nasini** and **Carrara**, *Gazz. chim. ital., 24, I,* 271 (1894); [d] **Brühl**, ***Ann.*, 235,** 1 (1886); [e] **Auwers, *Ber.*,** 44, 3690 (1912); [f] Bruhl, **J.** *prakt. Chem., [2]50,* 142 (1894); [g] Gennari, *Gazz. chim. ital., 24, I,* 253 (1894).

might be termed normal furan derivatives. The differences in the group, for the D line, vary from −0.134 to −1.078 and the average difference is −0.479. It is of interest to point out in this connection that the tetrahydro derivatives of furan show much less difference in the values of EMR than do the furan derivatives; e. g., five typical tetrahydrofuran derivatives showed differences from −0.31 to +0.03.[5]

In the second class are found all of the furan derivatives in which the side chain contains a double bond forming a conjugated system with the ring (Table I, 14–26). The differences in the group, for the D line, vary from $0.814 to +5.523. This result is not surprising in view of the many observations of optical exaltations caused by the presence of conjugated

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[5] Tetrahydrofuran. −0.13; 3-methyltetrahydrofuran, +0.03; **tetrahydrofurfuryl** alcohol, −0.16; **tetrahydrofurfural**, −0.31; **tetrahydrofuroic** acid, −0.11.

systems. Since all of these compounds exhibit absorption in the near ultraviolet region, the exaltations are probably caused by the proximity of this absorption band. It has previously been demonstrated that the refractive index increases rapidly as an absorption band is approached and apparently rises to infinity at the center of the band. The absorption spectra of a number of the furan derivatives used in this investigation are shown in Figs. 1 and 2.

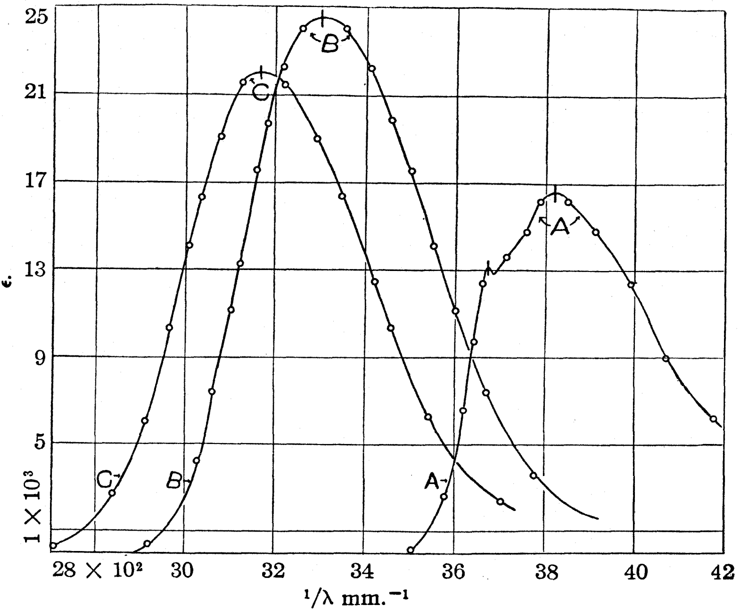

Fig. 1.—A, Furylethylene; B, ethyl furylacrylate; C, furylbutenone; solvent, ethyl alcohol.

In an effort to obviate the effect of the ultraviolet absorption bands it seemed of interest to make use of a proposal of Hunter.[6] He suggested that if the Sellmeir equation for dispersion (1) be used to calculate a value for the refractive index at a wave length sufficiently removed from the major absorption bands to be uninfluenced by them, the observed and calculated values would agree better than at visible wave lengths. By the use of three simultaneous equations, the constants for the following form of the Sellmeir dispersion formula were calculated for a number of furan derivatives.

$$n^2 = \frac{M}{\lambda^2 - \lambda_0^2} + C + 1 \qquad (1)$$

In this equation λ is the wave length of light used in the determination of n, λ_0 is the free vibrational period of the electron which is responsible

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[6] Hunter, *J. Chem. Soc.*, 123, 434, 1671 (1923).

for the refraction and also for the absorption of light, and M is an intensity factor. The value of λ_0 should represent an absorption band in the ultraviolet; that it does so has been verified experimentally for five of the compounds used (Table II). The calculated and observed values for the absorption bands were found to differ by only 250 Å., an effect which can be attributed to the influence of the solvent (alcohol).

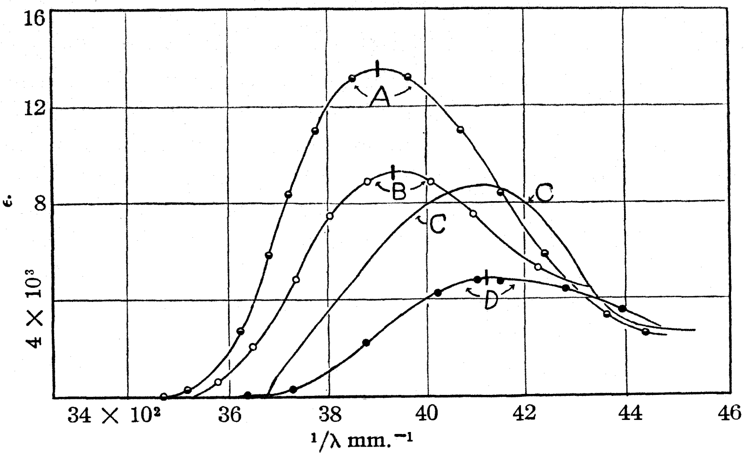

Fig. 2.—A, 5-Chlorofuroic acid; B, 3-chlorofuroic acid; *C*, 2-furoic acid; D, 2-methyl-3-furoic acid; solvent, ethyl alcohol.

TABLE II

ABSORPTION SPECTRA MAXIMA FOR FIVE DERIVATIVES OF FURAN

	Compound	Molecular extinction coefficient	Maxima in Å.	Sellmeir equation constant λ_0
1	Furylethylene	16600	2600	2325
2	Furylbutenone	22000	3100	2967
3	Furylpentenone	22800	3100	2888
4	Ethyl furylacrylate	24500	3000	2754
5	Furfural pinacolone	20500	3200	2983

In the above equation the first term will vanish if λ is taken to be infinite, and the square root of $(C + 1)$ will be the refractive index at infinite wave length. The exalting effect of the ultraviolet absorption band should therefore be at a minimum. The values obtained from these calculations at infinite wave length are shown in Table I. The results show that the differences are somewhat less than those at visible wave lengths but they are far too great to constitute any improvement in the situation.

The most satisfactory application of an empirical relation derived from refractive indices, to the study of structural problems has been made by

Auwers.[7] He uses the following calculation of the percentage exaltation of dispersion (E)

$$E = \frac{(\Sigma_\gamma - \Sigma_\alpha)\text{obs.} - (\Sigma_\gamma - \Sigma_\alpha)\text{calcd.}}{(\Sigma_\gamma - \Sigma_\alpha)\text{calcd.}} \times 100\%$$

$$\Sigma = \text{specific refraction} \times 100$$

This method was tried in the furan series for four pairs of isomeric alpha- and beta-substituted compounds. The values of E, listed in Table I, show that there is a very large difference between the alpha- and beta-isomers, and that the value for the alpha compound is always larger than that of the beta-compound. A comparison of the densities, boiling points, refractive indices and other properties indicates that the exaltation of the dispersion is unique in showing a marked difference between the isomers.[8] Although the differences in the percentage exaltation of the dispersion constitute a satisfactory means of distinguishing between the alpha- and beta-isomers, this method has the serious limitation of requiring that both isomers be available for comparison.

It was also observed that the constant M of the Sellmeir equation differs quite markedly in the alpha- and beta-derivatives of furan (see Table I). This constant is a value which, by deduction, represents the intensity of the vibration producing the absorption band and is directly related to the exaltations of the dispersion. In the compounds examined, the value of M was always higher for the alpha-isomer. This evidence of higher vibrational intensity in the alpha-isomers might be interpreted to mean that the alpha-derivative would be more reactive than the beta-derivative. With the present incomplete knowledge of the relative reactivity of substituents in the alpha- and beta-positions this interpretation cannot be confirmed from the chemical standpoint. This conclusion is in agreement with the observation that a halogen atom in the beta-position is less reactive than one in the alpha-position.

In its chemical behavior, in general, the furan ring occupies a position intermediate between the unsaturated aliphatics and the typically aromatic benzene ring. A comparison of the exaltations of the dispersion of corresponding benzene and furan derivatives (Table III) indicates a similarity in the compounds that have simple substituents (Cl, Br, CH_3). The effect of a substituent containing a double bond in the α,β-position of the side chain is much more marked in the furan series than in the benzene series. This result appears to parallel the unusual chemical behavior of furan derivatives with a double bond in the α,β-position of the side chain;

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[7] Auwers, Ber., 43,806 (1910); *Ann.*, 408,212 (1915); 422,160 (1921).

[8] The generalization made here is based on a comparison involving only a few pairs of alpha- and beta-isomers. It is our intention to synthesize a number of other beta-substituted furan derivatives in order to test the validity of this general statement.

these compounds readily undergo a scission of the ring, accompanied by an unusual rearrangement.[9]

Table III

Percentage Exaltation of Dispersion in Benzene and Furan Series

$E_{\Sigma\gamma} - \Sigma_\alpha$

Substituent	$-H$	$-Cl$	$-Br$	$-CH_3$	$-COOC_2H_5$	$-CH{=}CH_2$	$-CH{=}CH-COOC_2H_5$	$-CH{=}O$
Benzene series[a]	7	10	11	11	26	45	105	49
a-Furan series	−6	12[b]	10[b]	10	48	79	227[c]	110[c]

[a] The data for the benzene series are those of Auwers [*Ber.*, **45**, 2769 (1915); *Ann.*, **408**, 212 (1915)]. [b] Values for the 8-substituted furan derivatives are Cl, −3.77; Br, −12.4. [c] The values for the furan series are much higher than those of a simple ethylenic series. In the series, $CH_3CH{=}CH-$, the values are $-CH{=}O$, 55; $-CH{=}CH-COOC_2H_5$, 128 [Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **84**, 34, 108 (1911)]. The effect of ring closure on spectrochemical properties has been studied by Auwers [*Ann.*, **415**, 98 (1918); 422, 133 (1921)].

It is of interest to note that the model of benzene suggested by Dupont[10]. and by Latimer and Porter,[11] can be applied also to furan and other five-membered heterocyclic rings of aromatic character, such as thiophene, pyrrole and glyoxaline. The essential feature of this model is a "centric" system of six electrons, which in the benzene ring may be considered to be formed by a contribution of one electron from each carbon atom of the ring. In the case of furan the "centric" system is also one of six electrons, four of which may be considered to be contributed from the four carbon atoms and two from the oxygen atom (Fig. 3, I). The system in furan may then be represented by equilibria of the following types of electronic arrangements.

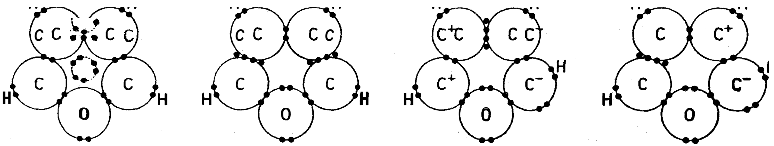

Fig. 3.—Electronic formulas fpr furan: I, centric formula; II, ethylenic formula; III, active form for 1,4-addition; IV, active form for 1,2-addition.

Active forms of furan may be postulated to explain either 1,2- or 1,4-addition (Fig. 3, III and IV) by use of the general conceptions of Carothers concerning the double bond.[12] A consideration of 1,4-addition to the furan ring will be presented in a later publication dealing with the mechanism of rearrangements in the furan series.[13]

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[9] Pummerer and Gump, *Ber.*, **56**, 999 (1923).

[10] Dupont, *Bull. soc. chim.*, [4] 41, **1334** (1927).

[11] Latimer and Porter, This journal, **52**, 206 (1930).

[12] Carothers, *ibid.*, 46, **2226** (1924).

[13] Reichstein, *Ber.*, **63**, 750 (1930); Runde, Scott, and Johnson, This journal, **52**, 1284 (1930). See also, Pummerer and Gump, *Ber.*, 56, **999** (1923).

Experimental

The furan derivatives used in this investigation were prepared with only minor deviations from methods which previously have been described in the literature. The final purifications were always carried out with consideration only of purity of the product, and not of yield. In Table IV are given the physical constants and references to the methods of preparation.

TABLE IV

PHYSICAL CONSTANTS OF COMPOUNDS

No.	Compound	Reierence	Boiling point, °C.
1	Furan	*a*	31_{745}
2	2-Methylfuran	*b*	63.1_{749}
3	Furfuryl alcohol	*c*	80_{19}
4	Furfuryl acetate	*d*	67_{8}; 180_{742}
5	Ethyl furylpropionate	*e*	101–10222
6	1-Furylbutane-3-one	f	95_{15}
7	1-Furylpentane-3-one	*g*	$88\ 5_{10}$
8	2-Chlorofuran	h	$77\ 5_{750}$
9	3-Chlorofuran	*h*	79_{742}
10	2-Bromofuran	*h*	$102\ 2_{750}$
11	3-Bromofuran	*h*	102.5_{743}
12	2-Methyl-3-carbethoxyfuran	*i*	49.5_{10}; 57_{17}
13	Ethyl furoate	*j*	128_{95}; m. p 34
14	Ethyl 5-chlorofuroate	k	88_{5}
15	Ethyl 3-chlorofuroate	k	217_{75}; m. p. 21.7
16	Furyl cyanide	1	146738
17	Furylethylene	*m*	94_{742}
18	1-Furyl-1-butene-3-one	*n*	116_{10}; m. p. 39.7
19	1-Furyl-1-pentene-3-one	*g*	128_{15}
20	Ethyl furylacrylate	o	$118–119_{10}$
21	Furfural pinacolone	*g*	120_{3}

[a] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 40. [b] Wolff, *Ann.*, 394, 101 (1912). [c] Wienhaus, *Ber.*, 53, 1657 (1920). [d] Zanetti, THIS JOURNAL, 47, 535 (1925). [e] Windaus and Dalmer, *Ber.*, 53, 2304 (1920). [f] Harries and Kaiser, *ibid.*, 32, 1320 (1899). [g] Kasiwagi, *Bull. Chem. Soc. Japan*, 1, *90* (1926); *Chemical Abstracts*, 20, 3004 (1926). [h] Shepard, Winslow and Johnson, THIS JOURNAL, 52, 2083 (1930). [i] Benary, *Ber.*, 44, 493 (1911). [j] Gennari, *Gazz. chim. ital.*, 24, I, 250 (1894). [k] Hill and Jackson, *Am. Chem. J.*, 12, 30, 36 (1890). [l] From the dehydration of furfuraldoxime, *cf.* Runde, Scott and Johnson, THIS JOURNAL, 52, 128 (1930). [m] Moureu, Dufraisse and Johnson, *Ann. chim.*, [10] *7*, 14 (1927). [n] "Organic Syntheses," Vol. VII, p. 42. [o] From the silver salt and ethyl iodide, *cf.* Gibson and Kahnweiler, *Am. Chem. J.*, 12, 315 (1890).

The method employed in the examination of the absorption spectra was that described by Orndorff, Gibbs and McNulty,[14] using a Hilger spectrograph in conjunction with a Hilger sector photometer. The light source was a high tension spark between brass electrodes under water.

The refractive indices were measured at five wave lengths and three dif-

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[14] Orndorff, Gibbs and McNulty, THIS JOURNAL, 47, 2767 (1925).

ferent temperatures, using a water-jacketed Pulfrich refractometer. The densities were determined in carefully standardized pycnometers of two and five cc. capacity. In Table V the numerical results are summarized and tabulated. In addition to these values, certain previously recorded values from the literature were used in making the calculations given in Table I.

TABLE V

REFRACTIVE INDICES FOR FURAN AND DERIVATIVES

No.	*Compound*	*t*, °C.	d^t_4	d*n*/d*t* × 10⁶	A6438	A5893	λ5790	λ5461	A4359
1	Furan	20	0.9366	62	1.4188	1.4214	1.4221	1.4243	1.4363
2	2-Methylfuran	20	.9132	56	1.4298	1.4335	1.4337	1.4358	1.4481
3	Furfuryl alcohol	20	1.1285	41	1.4820'	1.4848	1.4854	1.4879	1.5010
4	Furfuryl acetate	25	1.1131	42	1.4576	1.4603	1.4609	1.4631	1.4751
5	Ethyl furylpropionate	25	1.0527	52	1.4534	1.4569	1.4576	1.4585	14705
6	Furylbutanone	25	1.0258	42	1.4653	1.4697	1.4703	1.4725	1.4847
7	Furylpentanone	25	1.0029	44	1.4628	1.4670	1.4675	1 4697	1.4816
8	2-Chlorofuran	20	1.1922	52	1.4543	1.4571	1.4580	1.4604	1.4737
9	3-Chlorofuran	20	1.2098	54	1.4561	1.4589	1.4596	1.4619	1.4744
10	2-Bromofuran	20	1.6500	55	1.4927	1.4981	1.4988	1.5018	1.5173
11	3-Bromofuran	20	1.6605	50	1.4930	1.4962	1.4970	1.4996	1.5140
12	2-Methyl-3-carbethoxyfuran	25	1.0102	43	1.4140	1.4159	1.4163	1.4177	1.4252
13	Ethyl furoate	40	1.0974	48	1.4662	1.4699	1.4706	1.4738	1.4906
14	Ethyl 5-chlorofuroate	25	1.2418	44	1.4905	1.4944	1.4954	1.4987	1 5176
15	Ethyl 3-chlorofuroate	35	1.2408	42	1.4823	1.4857	1.4864	1.4894	1.5057
16	Furyl cyanide	20	1.0822	*50*	1.4757	1.4798	1.4808	1.4839	1.5032
17	Furylethylene	25	0.9316	60	1.4927	1.4981	1.4991	1.5039	1.5312
18	Furylbutenone	45	1.0572	54	1 5635	1.5788	1.5813	1.5909	1.6588
19	Furylpentenone	25	1 0685	50	1.5651	1.5787	1.5912	1.5901	1.6496
20	Ethyl furylacrylate	25	1.0891	50	1.5347	1.5459	1.5479	1.5548	1.6008
21	Furfuralpinacolone	25	1.0022	49	1.5373	1.5495	1.5513	1.5588	1.6124

Summary

1. The densities and refractive indices (in the visible region of the spectrum) have been measured for furan and twenty furan derivatives. The absorption spectra of eight furan derivatives are reported.

2. From the molecular refractions and the exaltations of the dispersion, calculated from these data, certain generalizations have been made concerning the effects of various types of substituents in the furan ring.

3. It has been shown that isomeric alpha- and beta-substituted furan derivatives may be distinguished from each other by spectrochemical means. The exaltations of the dispersion for the alpha-isomers are invariably higher than for the beta-isomers.

4. It has been shown for five furan derivatives that the wave lengths

of the absorption maxima (in the near ultraviolet) calculated from the Sellmeir dispersion formula are in agreement with the wave lengths of the absorption maxima actually observed.

5. Electronic formulas for the furan ring have been proposed and discussed briefly from the standpoint of interpretation of reactions of furan derivatives.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

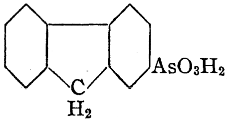
SOME ARSONIC ACIDS OF FLUORENE AND ITS DERIVATIVES

BY F. E. CISLAK[1] AND CLIFF S. HAMILTON

RECEIVED NOVEMBER 21, 1930 PUBLISHED FEBRUARY 9, 1931

In an attempt to find arsenicals which might be of value from the standpoint of chemotherapy, it seemed desirable to make a study of arsonic acids of fluorene and of some of its derivatives[2]

Bart's[3] method of preparing arylarsonic acids was adapted to the preparation of 2-arsonofluorene (I), 2-arsonofluorenone (II) and 2-acetamino-7-arsonofluorene (III). In the preparation of (III) the steps taken are indicated graphically below; the yield of (III) from (VI) was extremely low.



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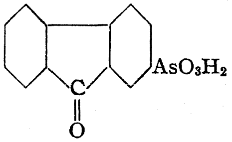

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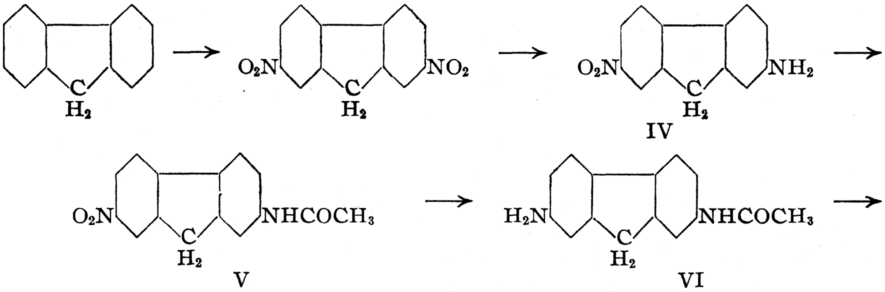

IV

V

VI

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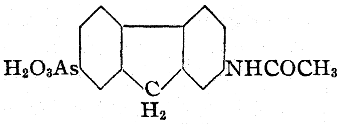
[1] This article is an abstract of Part II of a thesis submitted to the Graduate School of Northwestern University by F. E. Cislak in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The work was made possible by a grant from Parke, Davis and Company.

[2] Some of the compounds described in this article are being tested pharmacologically at the University of Wisconsin under the direction of Dr. **A.** L. Tatum, **but** no data are available at this time.

[3] Bart, Ann., **429,** 55 (1922).



III

2-Amino-7-nitrofluorene (IV) was first prepared by Diels.[4] By the nitration of 2-acetaminofluorene in glacial acetic acid, he obtained a mixture of 1-nitro-2-acetaminofluorene and 2-acetamino-7-nitrofluorene. This mixture could not be separated, but after hydrolysis the nitroaminofluorenes could be separated with difficulty. Because of the difficulty in obtaining any quantity of 2-acetamino-7-nitrofluorene by this procedure, a method was devised for the preparation of the desired substance in yields of 90–95% of the calculated amount.

The compounds, 2-acetamino-7-nitrofluorene, 2-acetamino-7-aminofluorene, as well as arsonic acids of fluorene have not been reported previously in the literature.

Experimental

2-Nitrofluorene and 2-Aminofluorene.—These compounds were prepared by the methods devised by Diels.[5]

2-Arsonofluorene.—Fifteen grams of 2-aminofluorene was mixed with 550 cc. of water, treated with 20 cc. of concd. hydrochloric acid solution and heated to boiling. The resulting clear solution was cooled (40°) rapidly, thereby causing the precipitation of the hydrochloride of 2-aminofluorene. While stirring this mass, a saturated aqueous solution of 6 g. of sodium nitrite was added dropwise. The hydrochloride of 2-aminofluorene then disappeared and a clear brownish yellow solution resulted. This solution was gradually heated to 60°, filtered hot and the filtrate cooled to 20°, causing the precipitation of golden yellow needles of fluorene diazonium chloride.

Thirteen grams of sodium meta-arsenite and 1 gram of copper sulfate were dissolved in 300 cc. of water. This solution was stirred during the entire course of the arsonation. In small portions, the mixture of solid fluorene diazonium chloride and its saturated solution was added to the arsenitc at room temperature. At once a vigorous evolution of nitrogen occurred. Sufficient 6 N sodium hydroxide solution was added from time to time to make this arsenite solution just alkaline. When all of the diazo compound had been added, the solution was stirred for fifteen hours. The mixture was then heated to 90° and stirred for three-quarters of an hour. It was filtered hot, and the filtrate acidified with 10 cc. of concd. hydrochloric acid solution, thereby precipitating 2-arsonofluorene. This precipitate was removed by filtration, washed with water, dissolved in a dilute solution of sodium carbonate, reprecipitated with hydrochloric acid and again separated by filtration, washed and dried; yield 4.5 g.

Anal. Calcd. for $C_{13}H_{11}O_3As$: As, 25.86. Found: As, 25.71, 25.81.

2-Nitrofluorenone and 2-Aminofluorenone.—The preparation of these compounds has been described by Diels.[6]

2-Arsonofluorenone.—Ninety cc. of concd. hydrochloric acid solution was added to one liter of water and the solution heated to 80°. Thirty grams of 2-aminofluorenone

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[4] Diels, *Ber.*, 35, 3284 (1902).

[5] Diels, *ibid.*, 34, 1758 (1901).

[6] Diels, *ibid.*, 34, 1864 (1901).

was added to the hot solution and while stirring this mixture, it was heated to 97° until all of the solid dissolved. The resulting golden-colored solution was quickly cooled to 50°; at this temperature, the golden needles of 2-aminofluorenone hydrochloride crystallized from the solution. While stirring this mixture, a saturated aqueous solution of 14 g. of sodium nitrite was added drop by drop. After all of the nitrite solution had been added, the mixture was stirred for fifteen minutes more and then cooled to 15°.

Twenty-five grams of sodium meta-arsenite and 2 g. of copper sulfate were dissolved in 400 cc. of water. While stirring the arsenite solution, the solution of fluorenone diazonium chloride was added in small portions. A vigorous evolution of nitrogen occurred. The procedure from this point was the same as outlined under 2-arsonofluorene; yield, 10 g.

Anal. Calcd. for $C_{13}H_9O_4As$: As, 24.67. Found: As, 24.60, 24.53.

2,7-Dinitrofluorene.—For the preparation of this compound the directions given by Morgan and Thomson[1] were followed.

2-Amino-7-nitrofluorene.—To a solution of 1800 cc. of 95% alcohol and 200 cc. of concd. ammonia was added 30 g. of 2,7-dinitrofluorene. This solution was maintained just below its boiling point and a stream of hydrogen sulfide was passed in for four hours. At the end of the first hour the solution changed its original yellow color to a deep red and a red solid began to crystallize from the solution. At the end of the four-hour reduction period, 250 cc. of water was added to the mixture and the latter cooled to about 10°. The red precipitate formed was removed by filtration. The 2-amino-7-nitrofluorene was isolated from this precipitate by boiling the latter with 16 liters of water to which had been added 1500 cc. of concd. hydrochloric acid solution. This solution was filtered hot, the filtrate cooled and then made alkaline by the addition of an excess of ammonia solution. The precipitated orange-red 2-amino-7-nitrofluorene was filtered, washed with water and then with 100 cc. of alcohol. It was dried at 100°; yield, 90–94%. Crystallization from alcohol gave a product melting at 228–229° (corr.).

When this compound was mixed with some 2-amino-7-nitrofluorene prepared by the method of Diels,[4] there was no change in melting point.

2-Acetamino-7-nitrofluorene.—Forty-five grams of 2-amino-7-nitrofluorene was dissolved in 400 cc. of hot glacial acetic acid. To this solution were added ten 25-cc. portions of acetic anhydride, the solution being stirred after the addition of each portion. When all of the acetic anhydride had been added, the solution was refluxed for eight hours and filtered hot, thereby removing a slight amount of dark brown sediment which had formed. To precipitate the bright yellow acetylated product, the filtrate was poured into four volumes of water. It was removed by filtration, washed with 25 cc. of hot glacial acetic acid, and dissolved in 600 cc. of hot glacial acetic acid. The acetic acid solution was boiled with decolorizing carbon, filtered and the resulting filtrate diluted with 50 cc. of water and cooled to about 10°. The 2-acetamino-7-nitrofluorene crystallized from this solution. It was removed by filtration, washed several times with water and finally with two 100-cc. portions of 95% alcohol; yield, 75% of the calcd. amount. Crystallization from alcohol gave a product melting at 250–253° (corr.).

Anal. Calcd. for $C_{15}H_{12}N_2O_3$: N, 10.46. Found: N, 10.18, 10.23.

2-Acetamino-7-aminofluorene.—Thirty grams of 2-acetamino-7-nitrofluorene was dispersed in 700 cc. of 95% alcohol. To this were added 50 cc. of water, 100 g. of zinc dust, and a solution of 5 g. of calcium chloride in 20 cc. of water. This mixture was refluxed for five hours under mechanical stirring and filtered hot to remove the excess

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[7] Morgan and Thomson, *J. Chem. Soc.*, 691 (1926).

zinc. This zinc was washed on the filter paper with 20 cc. of hot alcohol and then boiled with 200 cc. of 95% alcohol and separated from the alcohol by filtration. All the filtrates were combined and added to four volumes of water, thus precipitating white 2-acetamino-7-aminofluorene, which slowly acquired a gray color. This compound was removed by filtration and washed with water. In order to purify the resulting product, it was dispersed in I liter of hot water (90°) and to this was added 15 cc. of concd. hydrochloric acid solution, thus causing nearly all of the substance to go into solution. The mixture was filtered hot and the 2-acetamino-7-aminofluorene was reprecipitated from the filtrate by the addition of an excess of ammonia solution, filtered, washed with water and dried; yield, 60–65% of the calcd. amount. Upon recrystallization from alcohol, the compound decomposed at 188–192° (corr.).

Anal. Calcd. for $C_{15}H_{14}N_2O$: N, 11.74. Found: N, 11.66, 11.78.

2-Acetamino-7-arsonofluorene.—No satisfactory method has been found for preparing this substance. The method described below gave only small yields.

One liter of water was heated to 70° and to it was added 75 cc. of concd. hydrochloric acid and while stirring this solution, 15 g. of 2-acetamino-7-aminofluorene was added. The stirring at 70° was continued for fifteen minutes. Then the solution was cooled to 30° and while stirring, an aqueous solution of 6 g. of sodium nitrite was added drop by drop. After all of the nitrite solution had been added the solution was stirred for thirty minutes.

Fifteen grams of sodium meta-arsenite and a crystal of copper sulfate, the size of a pea, were dissolved in 200 cc. of water. The arsenite solution was stirred mechanically while the diazo solution was added in small portions. A copious evolution of nitrogen took place. After each portion of the diazo solution was added, the arsonation mixture was rendered just alkaline to litmus by the addition of 6 N sodium hydroxide solution. The solution was stirred for an hour and then the temperature was raised to 70–75°, and the stirring continued for another hour. At the end of this time the mixture was made strongly alkaline by the addition of 30 cc. of 6 N sodium hydroxide and filtered. The filtrate. upon acidification, gave a light brown precipitate, which was filtered off, dissolved in 300 cc. of a dilute sodium carbonate solution, filtered, acidified with concd. hydrochloric acid solution and the precipitate then formed removed by filtration and dried at 60°; yield, 2–2.5%; color; dull yellow.

Anal. Calcd. for $C_{15}H_{14}NO_4As$: As, 21.61. Found: As, 21.80, 21.49.

Summary

1. 2-Arsonofluorene, 2-arsonofluorenone and 2-acetamino-7-arsonofluorene have been prepared for the first time.

2. A method of preparing 2-acetammo-7-nitrofluorene in considerable amounts with good yields has been developed.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE ACETOACETIC ESTER CONDENSATION. II. THE REACTION OF ALIPHATIC ESTERS WITH SODIUM

BY JOHN M. SNELL AND S. M. MCELVAIN

RECEIVED NOVEMBER 26, 1930 PUBLISHED FEBRUARY 9, 1931

In a previous communication[1] from this Laboratory it was pointed out that in any study of the synthetic phase of the acetoacetic ester condensation the choice between sodium and sodium ethoxide as condensing agents was an important consideration for the reason that the metal reacts with the type of ester used in the condensation to form a distinctly different type of compound, *viz.*, the sodium derivative of an acyloin. The acyloin and related substances may be the major if not the sole products of reaction of certain esters with sodium. The results reported at that time showed that no such complications accompany the use of sodium ethoxide as a condensing agent.

Although a number of earlier investigators had observed that certain esters react with sodium to give compounds other than the acetoacetic ester type, it was Bouveault and Locquin[2] who first formulated the reaction as being two molecules of the ester and four atoms of sodium with the formation of the sodium salt of an acyloin which was converted by hydrolysis into the acyloin

$$2RCOOR' + 4Na \longrightarrow RC(ONa) = C(ONa)R + 2NaOR'$$

$$RC(ONa) = C(ONa)R \xrightarrow{H_2O} RC(OH){=}C(OH)R \longrightarrow RCHOHCOR$$

Bouveault and Locquin carried out the reaction between sodium and the ethyl esters of acetic, propionic, butyric, caproic, isobutyric and trimethylacetic acids at 0° in ether as a solvent. They obtained, after allowing the reaction to proceed for several days, quite good yields (in most cases approximately 80% of the theoretical) of the acyloins. There was generally a small amount of the diketone, RCOCOR, and some higher-boiling material obtained from the reaction. It was thought that the former compound resulted from the oxidation of the sodium derivative of the acyloin, and that the latter was produced from the acyloin during distillation. The only explanation of the mechanism of the reaction that was offered by these investigators is the one shown above. In 1920 Scheibler and Voss[3] offered an explanation for the formation of acyloins which postulated an intermediate formation of the sodium salt of the enol form of the ester. They stated that under the reaction conditions (0°) of Bouveault and Locquin the hydrogen which was given off during the formation of the enolate

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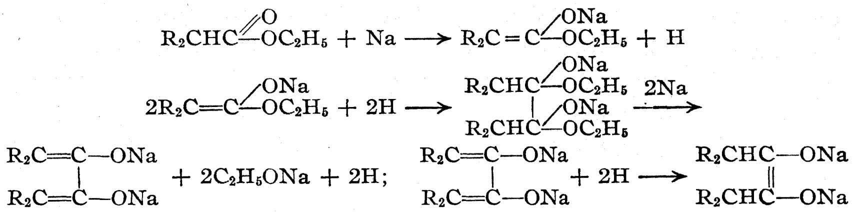
[1] McElvain, THIS JOURNAL, 51, **3124** (1929).

[2] Bouveault and **Locquin,** Bull. *soc. chim.,* [3] 35, 629 (1906).

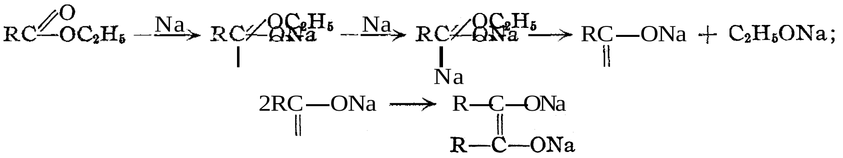
[3] Scheibler and **Voss,** *Ber.,* 53, **388** (1920).

salt was utilized to reduce this salt to the acyloin, but that at the temperature (the boiling point of ether) at which they prepared the salts of the enol forms of esters the hydrogen was evolved as such before it could cause the reduction of the enolate. This explanation hardly seems reasonable, since the results reported below show that excellent yields of the acyloins may be obtained at the temperature of boiling ether. Later, in 1923, Scheibler and Emden[4] reported a study of the formation of the acyloins and proposed the following mechanism for the reaction



It is seen that this mechanism also postulates the intermediate formation of a salt of the ester enolate. No reason was given for the necessity of assuming alternate addition and loss of hydrogen in the process.

One grave weakness[5] in this mechanism is that it will not explain the formation of an acyloin from such an ester as ethyl trimethylacetate which has no hydrogen on the carbon atom adjacent to the carbethoxy group and consequently cannot form an ester enolate. Scheibler and Emden handle such a case by postulating a special mechanism for this type, as follows



Such esters must go through a different mechanism, it is pointed out, on account of the slowness and incompleteness of the reaction.

Scheibler and Emden explained the presence of small amounts of the diketone, RCOCOR, which often accompanies the acyloin as resulting from the oxidation of salt of the di-enolate of the acyloin by air and pointed

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[4] Scheibler and Emden, *Ann.,* 434,265 (1923).

[5] Another may be noted. Scheibler and Emden point, in a footnote, to an observation of Bouveault and Blanc that only esters which have at least one hydrogen on the α-carbon atom may be reduced by sodium and alcohol to the corresponding alcohol as further substantiation of their mechanism. This "generalization" is based, apparently, on the behavior of ethyl benzoate and has the common defect of such "generalizations," *viz.*, that it is not generally applicable. For example, Courtot [*Bull. soc. chim.,* 35, 121 (1906)] has reported the reduction of ethyl Δ^3-2,2-dimethylbutyrate, $CH_2{=}CHC(CH_3)_2COOC_2H_5$, to the corresponding alcohol and his results have been confirmed by Folkers and Adkins in this Laboratory, who obtained a 61% yield of this alcohol by the reduction of the above ester with sodium and alcohol.

out that the potassium salts were much more susceptible than the sodium salts to such oxidation.

Recently Corson, Benson and Goodwin[6] described a general procedure for the preparation of a number of aliphatic acyloins. They obtained yields, approximately 50% of the theoretical, of products with 25° boiling range using boiling ether as a solvent. They noted the formation of the higher-boiling products which they felt were derived in part, at least, from the acyloins during distillation and also the diketones the formation of which they ascribed, as did Scheibler and Emden, to the oxidation of the salt of the di-enolate of the acyloin.

In the work which is now reported a study has been made of the reaction between sodium and the following esters: ethyl acetate, ethyl propionate, ethyl butyrate, ethyl isobutyrate and ethyl trimethylacetate. Ether, benzene and an excess of the ester were used as solvents. The temperature of each reaction was determined by the boiling point of the particular solvent used. In the cases when the two inert solvents were used one mole of the ester was allowed to react with two atoms of sodium. A number of different procedures for the decomposition of the sodium salts in the reaction mixture were tried, and it was soon discovered that considerable attention had to be given to this point if consistent and comparable results were to be obtained. The procedure finally adopted used the calculated amount of 35% sulfuric acid for the decomposition of these salts. This amount and concentration of sulfuric acid, besides destroying the alkalinity of the reaction mixture rapidly, converted all of the sodium which had been used into the solid $Na_2SO_4 \cdot 10H_2O$ from which the supernatant liquid could be directly decanted. The products of each reaction were separated into an acidic and neutral fraction by extraction of the former with a sodium carbonate solution. These two portions were then dried and subjected to fractional distillation.

Experimental Part

Materials Used.—The esters, ethyl acetate, ethyl propionate, ethyl butyrate, ethyl isobutyrate and ethyl trimethylacetate were carefully purified and dried by the procedure previously described (Ref. 1) in the first paper of this series. The ether and benzene (thiophene free) were distilled from phosphorus pentoxide before use.

General Procedure.—Two gram atoms of sodium was powdered by heating and vigorous stirring under xylene in a 3-liter flask fitted with a stirrer, reflux condenser and a dropping funnel. The xylene was then cooled and decanted from the sodium. The sodium was washed several times with dry ether to remove the xylene and finally covered with 600–800 cc. of ether. To this ether suspension of sodium 1 mole of the ester was added and the mixture stirred and refluxed until the reaction appeared to be complete.

There was a very noticeable difference in the reactivity of the various esters with powdered sodium in ether. In the case of ethyl acetate twenty-four hours of refluxing was required to complete the reaction. Ethyl propionate reacted quite completely

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[6] Corson, Benson and Goodwin, THIS JOURNAL, 52, 3988 (1930).

after about two hours of refluxing. In the case of ethyl butyrate, ethyl isobutyrate and ethyl trimethylacetate, the reaction was so vigorous that it could not be controlled if the ester were added in a single portion. For this reason the ester was added gradually from a dropping funnel at such a rate as to keep the ether boiling vigorously. The reaction of each of these three higher esters appeared to be complete in one to one and one-half hours. The reaction converted the sodium into a voluminous, amorphous, yellow, insoluble solid. A very noticeable feature of the reaction of ethyl trimethylacetate was that considerable sodium remained unreacted even after two hours of refluxing, while with each of the other esters practically all of the sodium was used up. The reaction, however, was complete so far as the ester was concerned for practically no unchanged ethyl trimethylacetate was recovered from the reaction mixture.

After the reaction was finished the calculated quantity of 35% sulfuric acid for neutralization of the sodium that had been used was added from the dropping funnel. During this addition the Bask was cooled with ice and the contents vigorously stirred. It required about five or ten minutes to complete this neutralization. The sodium sulfate with its water of crystallization readily separated and solidified in the bottom of the reaction flask. The supernatant liquid was decanted, the precipitate washed with 200 cc. of ether and the combined ether solutions extracted with a 20% solution of sodium carbonate. The carbonate extract was then acidified with sulfuric acid and extracted several times with ether. After drying, the ether extract of the acidic products and the original ether solution of the reaction products were fractionated.

A procedure similar to that outlined above was followed with benzene as the solvent instead of ether. Under these conditions of reaction the esters showed the same variation in reactivity that they did in the ether solution. Ethyl acetate was not used with benzene as the solvent on account of the rather uncertain results which it gave in ether solution. A considerable amount of unreacted sodium remained after the reaction of ethyl trimethylacetate in benzene as was the case in the ether solution.

The amounts and types of reaction products obtained from the reaction of these esters with sodium in the inert solvents, ether and benzene, are summarized in Table I. A ferric chloride test applied to a portion of the ether or benzene solution of reaction products before distillation indicated that small amounts of β-ketonic esters, resulting from an acetoacetic ester condensation, had been formed from ethyl acetate and ethyl propionate, but after distillation there was no evidences of such products in any of the fractions. Presumably the distillation had destroyed their identity so far as the ferric chloride test could determine and converted them into higher-boiling materials through condensation with other products of the reaction. The acidic products shown in the last two columns were obtained from the sodium carbonate extraction of the ether or benzene solution of the reaction products after the sodium salts of the reaction mixture had been decomposed and the $Na_2SO_4 \cdot 10H_2O$ filtered off. The calculations of the percentage yield of the diketone and acyloin are based on the amount of ester which was put into the reaction.

A very noticeable difference in reactivity of these esters with sodium was noted when an excess of the ester was used as the solvent. In these cases four to five moles of the ester was reacted with **23** g. (1 atom) of powdered sodium. The sodium could be covered directly with ethyl ace-

TABLE I

THE PRODUCTS OF REACTION BETWEEN SODIUM AND CERTAIN ALIPHATIC ESTERS IN ETHER AND BENZENE SOLUTION

Ester, ethyl	Amount used, g.	Solvent	Yield of RCOCOR[a]		Yield of RCHOHCOR[b]		Yield of higher boiling products,[c]	Yield of RCOOH,	Yield of higher acids,
			g.	%	g.	%	g.	g.	g.
Acetate	88	Ether	3	7	10	23	10	2	7
Propionate	102	Ether	5	9	30	52	14	...	...
Butyrate	116	Ether	5	7	52	72	7	3	...
Isobutyrate	116	Ether	3	4	54	75	2	4	4
Trimethylacetate	100	Ether	21	32	41	62	..	...	...
Propionate	102	Benzene	4	7	17.5	30	19	1	3
Butyrate	116	Benzene	5	7	44	61	13	3	2
Isobutyrate	116	Benzene	6	8	48.5	68	3	4	9
Trimethylacetate	50	Benzene	5	15	20	63	..	3	...

[a] This fraction was composed of material boiling higher than the ester and lower than the acyloin and represented approximately a 40° range. The major portion of this fraction in the case of ditrimethylacetyl boiled over a 10° range. It had the deep yellow color characteristic of the 1.2-diketones.

[b] This fraction had a boiling range of 5–10°. The highest boiling acyloin boiled under 100" (15 mm.).

[c] This fraction represents the material boiling higher than the acyloin and which had not reacted with sodium carbonate. It boiled as high as 200" (15 mm.). A small amount of undistillable residue was obtained from the ethyl acetate and ethyl propionate reactions.

tate or ethyl propionate and very little reaction appeared to take place until heat was applied. The reaction in either case was in no sense vigorous and it was necessary to reflux the ester for about two hours before the sodium had disappeared. The reaction mixture appeared quite homogeneous. With the three higher esters it was necessary to add the sodium in small portions to the ester. This was done by dipping the powdered sodium which was kept covered with dry ether with a dipper having a perforated bottom (constructed from a Gooch crucible) and allowing most of the ether to drain off before the addition of the sodium to the ester. The heat of reaction was sufficient to sustain refluxing until all of the sodium had reacted. The reaction mixture appeared as a thick pasty mass. The reaction products were isolated as described above and are summarized in Table II. The calculations of the yields of the various products were based on the amount of sodium *(23* g. in each case) that was put into the reaction.

Some Properties of the Diketones and Acyloins. The Diketones.—With the exception of ditrimethylacetyl, the diketones were obtained in quite small yields from the above reactions. They are characterized by their deep yellow color. They generally boil about 20–25° lower than the acyloin and about the same amount higher than the esters from which they are derived.

TABLE II

THE PRODUCTS OF REACTION OF SODIUM WITH AN EXCESS OF CERTAIN ALIPHATIC ESTERS

Ester, ethyl	Yield of RCOCOR[a] g.	%	Yield of RCHOHCOR[b] g.	%	Yield of β-keto ester[c] g.	%	Yield of higher boiling products, g.	Yield of RCOOH[d] g.	%	Yield of higher acids, g.
Acetate	...	...	..	..	46[e]	35	6[e]	14	23	3
Propionate	...	...	..	..	51"	32	15[e]	14	19	3
Butyrate	6[f]	8	2.5[f]	7	..	..	23	48	55	20
Isobutyrate	5	7	20	56	..	..	13.5	51	58	5
Trimethyl acetate	...	...	42	98	..	..	6	46	45	..

[a] Percentage yield calculated on the basis of 2Na producing 1RCOCOR. [b] Percentage yield calculated on the basis of 4Na producing 1RCHOHCOR. [c] Percentage yield calculated on the basis of 1Na producing $1RCOCHR'COOC_2H_5$. When, however, the alcohol was distilled out of the reaction of ethyl acetate and sodium a 72% yield of acetoacetic ester was obtained. [d] Percentage yield calculated on the basis of 1Na producing 1RCOOH. [e] Colorless, water-white liquids. [f] Deep yellow-colored liquids.

They are readily polymerized and rearranged by sodium ethoxide, as is shown by the following experiment. A solution of 9 g. of dibutyryl in 50 cc. of benzene was heated for two hours on a water-bath with 5 g. of sodium ethoxide. The reaction mixture was then acidified with sulfuric acid and separated into a neutral and acidic portion by extraction with sodium carbonate. The former portion yielded on fractionation 1 g. of unchanged dibutyryl and 4 g. of higher-boiling material. The acidic portion was separated by fractionation into 2 g. of butyric acid and 1 g. of di-n-propylglycolic acid,[7] m. p. 76°, neutral equivalent 166. Di-isobutyryl showed a similar behavior except that about 2 g. (18% of the calcd.) of di-isopropylglycolic acid,[8] m. p. 108–110°, neutral equivalent 163, was obtained. A similar experiment using 10 g. of ditrimethylacetyl yielded 7.5 g. of unchanged diketone, 1 g. of trimethylacetic acid and 1 g. of an undistillable tar.

The Acyloins.—The acyloins which are reported in Tables I and II were collected over a 5–10' boiling range. Acetoin boiled at 140–150°, propionoin at 160–170°, butyroin at 85–95' (12 mm.), isobutyroin at 175–180°, pivaloin (hexamethylacetoin) 80–90° (15 mm). The latter compound solidified on cooling and melted at 80–81°. All of the acyloins as obtained from the reaction show a yellow coloration which is much less intense than that characteristic of the diketones. This color is no doubt due to the presence of small quantities of the diketone.

In contrast to the diketones the acyloins are hardly affected by sodium

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[7] Cf. Crichton, *J. Chem. Soc.*, 89, 933 (1906).

[8] *Cf.* Barylowitsch, *Ber.*, 28,2465 (1895); Claisen, *Ann.*, **297**, 96 (1897); Scheibler, *ibid.*, **434,284 (1923).**

ethoxide; for example, 8 g. of isobutyroin was recovered unchanged when 10 g. of this acyloin was refluxed with 5 g. of sodium ethoxide in benzene solution. These reaction conditions, it was pointed out above, readily polymerized and rearranged the diketones with the exception of ditrimethylacetyl.

Bouveault and Locquin[2] thought that the higher-boiling products of the reaction were derived from the acyloin by polymerization during distillation. However, samples of propionoin, butyroin and isobutyroin after one and one-half hours of boiling under a reflux condenser were found to distil completely over the temperature range at which they had originally boiled. It would seem quite certain from this fact that the higher-boiling products owe their origin to some other source.

The Higher-Boiling Products.—Very little investigation was made on the nature of these products. With the exception of those obtained from ethyl acetate and ethyl propionate when an excess of the ester was used as the solvent (Table II), these products all possessed the yellow color suggestive of the diketone structure. The product from ethyl propionate (Table I) did not show any appreciable reduction with hydrogen in the presence of either catalytic platinum or nickel (propionoin was reduced quantitatively with the latter catalyst at 50° and under 150 atmospheres of hydrogen[9] to the 3,4-hexanediol). The product from ethyl propionate reacted with acetic anhydride in the ratio of 307 g. of the former to one mole of the anhydride. With the similar product from ethyl butyrate the ratio was 500 g. to one mole of the anhydride. They showed no reaction with semicarbazide but with phenylhydrazine a red viscous liquid was formed.

The Acidic Reaction Products.—The origin of that portion of the acidic reaction products representing the acid, the ester of which was used in the reaction, is discussed below. From the higher-boiling acidic products there were obtained, in the cases of ethyl butyrate and ethyl isobutyrate, small yields of di-n-propylglycolic acid and di-isopropylglycolic acid. These acids were obtained by recrystallization of fractions which boiled at 140–170° (15 mm.). After this fraction was removed the bulk of the higher acidic portion remained as an undistillable residue. This residue was no longer soluble in alkali. The dialkylglycolic acids are formed, as shown above, from the rearrangement of the diketones with sodium ethoxide and this reaction is, no doubt, responsible for their presence in the reaction mixtures obtained from ethyl butyrate and ethyl isobutyrate. The undistillable residue after the removal of the dialkylglycolic acid, since it was insoluble in alkali, was quite probably a lactide resulting from the heating of the α-hydroxy acids.

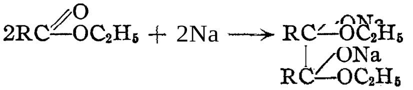
[9] This work was done by Mr. Karl Folkers under the direction of Professor Homer Adkins in this Laboratory.

Discussion of the Experimental Results and the Mechanism of the Reaction between the Esters and Sodium

An inspection of the data presented above shows that there is no perceptible difference in the rate at which the three esters, ethyl butyrate, ethyl isobutyrate and ethyl trimethylacetate react with sodium nor is there any great difference in the completeness with which they react in the inert solvents to form diketones and acyloins. The need, therefore, of a special mechanism to account for the slowness and incompleteness of reaction of those esters which cannot enolize does not exist, for ethyl trimethylacetate reacts somewhat more completely and just as rapidly as the other two. Corson, Benson and Goodwin[6] made a somewhat similar observation on the behavior of ethyl dimethylethylacetate. Since the only group capable of reaction that these three esters have in common is the carbethoxy group it is logical to conclude that the reaction of sodium with such esters involves only this particular group. The postulate of Scheibler and Emden that the reaction proceeds, when possible, through the salt of the enol form of the ester, or, when this is not possible, through an entirely different mechanism, has no experimental support and would seem to be quite unnecessary, if not erroneous.

It is also evident from the experimental data presented in Table I that the diketone is an intermediate product in the formation of the acyloin rather than the result of an oxidation of the acyloin as previous investigators of the reaction have thought. Egorova[10] arrived at a similar conclusion in his study of the action of sodium on the chloride of trimethylacetic acid. It would be difficult to explain the relatively high yields of the diketone in the case of ethyl trimethylacetate in Table I on the basis of atmospheric oxidation when the reaction conditions were practically identical to the conditions used with the other esters and ***unreacted*** sodium ***remained*** in the reaction mixture. The fact that dibutyryl and di-isobutyryl are readily polymerized and rearranged by sodium ethoxide while the ditrimethylacetyl is quite stable to this reagent is not without significance and indicates that the low yield of the former two is due to their partial destruction by the sodium ethoxide produced in the reaction.

It would seem, therefore, logical and consistent with the experimental facts to represent the reaction between sodium and such aliphatic esters as taking place in two steps. First, the formation of a diketone–sodium ethoxide addition product by the reaction of two molecules of the ester with two atoms of sodium



$$2RC(=O)OC_2H_5 + 2Na \longrightarrow \begin{array}{l} RC(ONa)OC_2H_5 \\ | \\ RC(ONa)OC_2H_5 \end{array}$$

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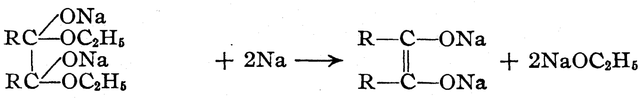
[10] **Egorova,** ***J. Russ. Phys.-Chem. Soc., 60,*** 1199 (1928); ***Chem. Abstracts,*** 23, 2935 (1929).

This reaction may involve the intermediate formation of a free radical, $R\underset{\overset{|}{\cdot}}{C}(OC_2H_5)ONa$, such as Blicke[11] noted in the reaction of benzaldehyde, phenyl benzoate and ethyl benzoate and sodium. This diketone–sodium ethoxide addition product is then converted by two more atoms of sodium into the sodium salt of the acyloin and sodium ethoxide



$$\begin{array}{l} RC{\diagup}^{ONa}_{OC_2H_5} \\ \ | \\ RC{\diagup}^{ONa}_{OC_2H_5} \end{array} + 2Na \longrightarrow \begin{array}{c} R—C—ONa \\ \| \\ R—C—ONa \end{array} + 2NaOC_2H_5$$

Whether or not the addition product reacts directly with the sodium or first loses sodium ethoxide to allow the free diketone to react with the sodium cannot be decided from any experimental data now available. Egorova[10] has shown that the latter reaction (between the diketone and sodium) does take place with ditrimethylacetyl.

The mechanism of Scheibler and Emden, it might be pointed out, allows for the intermediate formation of diketone–sodium ethoxide addition product in those cases in which the ester involved may enolize. Their mechanism, however, for the reaction of such esters as ethyl trimethylacetate, from which the intermediate formation of the diketone is so apparent in Table I, does not involve this intermediate, and is obviously inadequate.

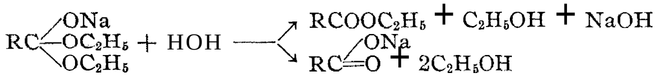
Table II shows that with an excess of ester as the solvent the acetoacetic ester condensation takes place with ethyl acetate and ethyl propionate. Judging from the color of the reaction products, no products of the diketone or acyloin type were formed. With ethyl butyrate very little of the diketone and acyloin, but considerable higher-boiling material with the characteristic yellow color of the diketones is produced. With ethyl isobutyrate the combined yield of di-isobutyryl and isobutyroin is only about 13% lower than those obtained when benzene was used as the solvent but it is seen that the amount of higher-boiling material is correspondingly higher. The very high yield of the acyloin and the absence of any diketone in the case of ethyl trimethylacetate must be due to the favorable conditions for the reaction when the ester is used as the solvent.

The source of the higher-boiling materials is a matter of speculation. It is the opinion of the authors that they are not derived from the acyloin during distillation for the reason, mentioned above, that the acyloin appears to remain practically unchanged after a period of boiling. The fact that the diketones are readily polymerized and rearranged by sodium ethoxide indicates that they are responsible, to some extent at least, for the presence of the higher-boiling materials in the reaction mixture. It is significant that very little or no higher-boiling products are obtained from ethyl trimethylacetate, the diketone of which is quite stable to sodium ethoxide. Added to this probability is the possibility of Claisen condensa-

[11] Blicke, THIS JOURNAL, 47, 229 (1925).

tions between an ester molecule and the diketone or acyloin induced by the sodium ethoxide formed in the reaction in the cases of those esters possessing a structure (two hydrogens on the a-carbon atom) capable of undergoing such a condensation. The fact that ethyl butyrate in Table II shows higher-boiling products almost to the exclusion of the acyloin while ethyl isobutyrate and ethyl trimethylacetate produce quite high yields of the acyloin type would seem to lend support to this latter suggestion.

The high yields of the acids, RCOOH in Table II, are striking. Previous investigators have noted the formation of such acids. Egorova[10] thought that the trimethylacetic acid which he obtained from the action of sodium on trimethylacetyl chloride resulted from the decomposition of the intermediate diketone, ditrimethylacetyl, by alkali. The data in Table II, particularly for ethyl trimethylacetate, show that such an explanation is insufficient for it is seen that practically all (98%) of the sodium put into the reaction was used in the formation of the acyloin and that no diketone could have been present. Still a 45% yield of the acid was obtained. Scheibler and Marhenkel[12] suggested that the acid resulted from one type of hydrolysis of the salt of the ortho ester thus



$$RC\begin{cases}ONa\\OC_2H_5\\OC_2H_5\end{cases} + HOH \longrightarrow \begin{cases}RCOOC_2H_5 + C_2H_5OH + NaOH\\ RC\begin{cases}ONa\\O\end{cases} + 2C_2H_5OH\end{cases}$$

This explanation involves the reaction of the sodium ethoxide produced in the reaction with a portion of the ester which is in excess of that required for the primary reaction and is supported by the fact that high yields of the acid, RCOOH, were obtained in each case when an excess of the ester was used as the solvent. In order to check this possibility, 68 g. of sodium ethoxide was refluxed with 380 g. of ethyl butyrate for thirty minutes. The reaction mixture after cooling was treated with the calculated amount of 35% sulfuric acid as was done in each of the above experiments. A yield of 49 g. (56% based on the sodium ethoxide) of butyric acid was obtained from the sodium carbonate extract.

It is apparent from the data presented above that sodium produces two distinct types of reaction with aliphatic esters, the acetoacetic ester condensation and the acyloin type of condensation. Whether or not the metal is directly responsible for the former type of reaction cannot be definitely decided from any experimental facts now known. There is no doubt, however, that the metal is the direct cause of the acyloin condensation and the simultaneous production of sodium ethoxide. It is quite probable that it is this latter compound that is responsible for any acetoacetic ester type of condensation which may take place. Obviously the alcohol produced in this latter condensation would react with the metal to produce more of the active condensing agent. Such a functioning of the sodium has been

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[12] Scheibler and Marhenkel, *Ann.*, **458**, 8 (1927).

previously suggested by Higley.[13] Some significance, therefore, may be attached to the fact that those esters, ethyl acetate and ethyl propionate, which are the most sluggish in their reaction with sodium in the inert solvents, react through the acetoacetic ester condensation when an excess of the ester is the solvent.

Summary

1. The reaction of ethyl acetate, propionate, butyrate, isobutyrate and trimethylacetate with sodium has been studied under various conditions.
2. The mechanisms which have been proposed for the formation of acyloins are discussed on the basis of the experimental results obtained.

MADISON, WISCONSIN

[COMMUNICATION NO. 449 FROM THE KODAK RESEARCH LABORATORIES]

A HEAT COAGULABLE PROTEIN FROM GELATIN

BY S. E. SHEPPARD, J. H. HUDSON AND R. C. HOUCK

RECEIVED DECEMBER 1, 1930 PUBLISHED FEBRUARY 9, 1931

In a report on the specification of a standard gelatin[1] attention was called to the desirability of specifying the permissible amount of heat coagulable protein in a standard gelatin. The presence of albuminous substances in gelatin has been frequently indicated, especially in articles dealing with its manufacture and purification.[2]

The following is an account of some preliminary work on the estimation, separation, and analysis of the heat coagulable protein from a number of different gelatins.

The results are insufficient to decide whether the substance is a single homogeneous protein or a mixture. They do, however, definitely establish its nature, in gelatin, as a foreign impurity of different constitution and composition.

Experimental

In separating the coagulable protein from gelatin it is found necessary first to adjust the P_H of the gelatin, with acetic acid, to near the isoelectric point of gelatin. Fifty grams of a gelatin with a P_H range of 5.9 to 6 dissolved in 800 cc. of water will require about 5 cc. of glacial acetic acid to bring the P_H to 4.7. Heating overnight on a steam-bath at a temperature of 80 to 100° is sufficient to hydrolyze the gelatin and allow the protein to

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[13] Higley, *Am. Chem. J.*, 37, 302 (1907).

[1] Hudson and Sheppard, *Ind. Eng. Chem.*, 21, 263 (1929), "A Contribution to the Preparation of Standard Gelatin," Communication 364. Davis, Sheppard and Briefer, *ibid.*, Anal. Ed., *1*, 56 (1929). "Specifications for Gelatin Standards."

[2] Bogue, "Chemistry and Technology of Gelatin and Glue," McGraw-Hill Book Co., Inc., New York, 1922, 1st ed.; Sheppard. "Gelatin in Photography," Monograph No. 1 from Kodak Research Laboratories, Rochester, New York, 1923, p. 131,

coagulate. Fifty grams of a de-ashed gelatin (PH4.9) in 800 cc. of water is treated with only 0.5 cc. glacial acetic acid and heated to effect coagulation.

The clear gelatin solution is decanted off through a coarse filter paper and the coagulum is broken up in the beaker by a stream of hot water, after which it is washed into the filter. Washing with hot water is continued until all the gelatin solution is removed from the coagulated protein. The protein is finally collected in the cone of the filter and then transferred, with a stream of water, to a weighing bottle. The water is evaporated off and drying completed in the oven at 105 to 110°. The amounts of coagulable protein were determined in various gelatins and the protein was analyzed for nitrogen.

TABLE I

ASH AND WATER FREE BASIS

Gelatin	Protein, %	Percentage N on protein	Origin
X1	0.37	14.6	Domestic calfskin, dc-ashed
X2	.63	14.6	Same
Y1	.27	12.0	Foreign calfskin, not de-ashed
X3	.62	14.6	Domestic calfskin, not de-ashed
W1	.40	13.7	Domestic bone, not de-ashed
X4	.22	11.0	Domestic hide, not de-ashed

For comparison, the whites of eggs were beaten up in water, filtered and analyzed.

TABLE II

ANALYTICAL DATA

	Egg whites	Coagulable protein from X2 gelatin
Ash, %	*3.7*	0.04
Inorganic S, %	0.24	0.00
Total S, %	1.54	.80
Labile S, %	0.49	.00063
Nitrogen, %	14.42	14.6

Isoelectric Point of Coagulated Proteins.—The material is obtained in coarse flocks, which are insoluble in water and in weakly acid and alkaline solutions Methods of determining the isoelectric point by desolvation are not, therefore, applicable. Neither was the form of the material suitable for cataphoretic determinations, although it is believed that we have now available a method for rendering it suitable, and this will be tried in later work. The method used was that of electro-endosmose, the inverse of electrophoresis. In this process, liquid is moved under the influence of a potential instead of the particle. A porous plug is formed of the material and brought between the two electrodes. Solutions of known PH are put in contact with the plug and the direction of flow of liquid through the plug is observed under an applied potential difference. The plug assumes a charge on coming into contact with the solution, the nature of the charge, positive or negative, depending on the PH of the solution and the isoelectric point of the material. The liquid in contact becomes oppositely charged, an electrical double layer being set up. By setting up a potential across the plug this layer is disturbed and liquid flows in one direction or the other; if on the alkaline side of the isoelectric point it flows toward the cathode, and if on the acid side toward the anode.

The apparatus employed was similar to that described by Briggs, Bennett and Pierson.[3] It is shown diagrammatically in Fig. 1, but it differs from that of Briggs in that the part which contains the plug is separable from the rest of the apparatus. This was found to be necessary because of the nature of the material used, since a satisfactory plug could not be obtained by filtering, as was done by Briggs and his co-workers. It was also desired to remove any doubt which might be cast on the results as being due to the presence of cotton or glass wool supporting the plug.

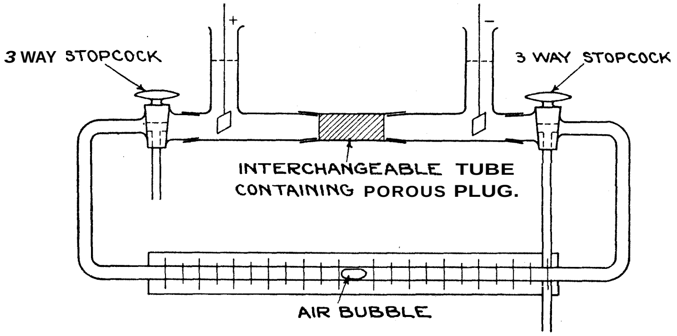

Fig. 1.—Electro-endosmose apparatus.

Accordingly the center portion of the apparatus was made an interchangeable unit in a centrifuge tube; the plug was formed by centrifuging, and then the plug along with the supporting tube was placed in the endosmose apparatus. Satisfactory plugs were obtained in this manner. The material was stirred up with the buffer to be used before centrifuging.

The plug having been formed and placed in position, the buffer of known PH, with which the material had been stirred before centrifuging, was poured into the apparatus and all air bubbles were removed by tilting the apparatus. A loose plug was then tested for by closing both stopcocks and pouring in more buffer on one side and watching the levels in the anode and cathode compartments. If the levels remained stationary the experiment was continued. If not, a new plug was formed. The stopcocks were opened and after the levels had become stationary the current was turned on. In most of the experiments a potential of 110 volts was applied across the plug. The direction of flow was observed and in cases where possible

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[3] T. R. Briggs, H. S. Bennett and H. L. Pierson, *J. Phys. Chem.*, **22**, **256** (1928)

the rate of flow determined. The direction of the current was then reversed and direction of flow and rate checked.

TABLE III

ISOELECTRIC POINT OF EGG ALBUMEN COAGULATED BY HEAT

Pa of buffer	Direction of flow through plug	Rate of flow, cm./min.
5.4	Cathodic	0.74
5.0	Cathodic	.10
4.8	Cathodic	.007
4.6	Anodic	.006
4.2	Anodic	.30
3.8	Anodic	.51

Clark and Lubs buffers, potassium acid phthalate with varying amounts of hydrochloric acid or sodium hydroxide, were employed. The *PH* values of a number of these were checked electrometrically and found to be satisfactory.

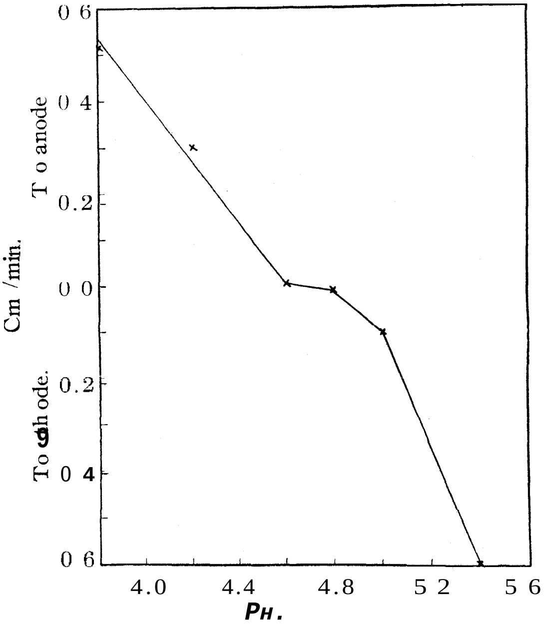

Fig. 2—Isoelectric point of egg albumen denatured by heat.

Egg Albumen.—The results obtained with egg albumen denatured by heat are shown by Table III and Figure 2.

The egg albumen was precipitated by heating from a 4% solution of dialyzed material.

The results indicate a value of *PH* 4.7 as the isoelectric point of egg albumen denatured by heat. The values of the isoelectric point of genuine egg albumen vary: from a *PH* of 4.7 as found by Loeb[4] and by Reinders and Bendien,[5] to a *PH* of 4.8 as found by Svedberg and Tiselius,[6] and to a PH of 4.95 as found by Abramson[7] and by Prideaux and Howitt.[4]

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[4] J. Loeb. "Proteins and the Theory of Colloidal Behavior," Chapt. 8, "Membrane Potentials," McGraw-Hill Book Co., New York, 1922, pp. 120–150. Prideaux and Howitt, *Proc. Roy.* Soc. (London), 126, 126 (1929). (Calculated from Loeb's figures of membrane potentials.)

[5] W. Reinders and W. M. Bendien, *Rec. trav. chim.*, 47, 977 (1928).

[6] T. Svedberg and A. Tiselius, THIS JOURNAL, 48, 2272 (1926).

[7] H. A. Abramson, *ibid.*, 50, 390 (1928).

Thus, it seems fairly safe to say that the isoelectric point of egg albumen is not appreciably changed by being denatured by heat.

Protein Coagulated from Gelatin Sols by Heat.—The isoelectric point of the material coagulated from gelatin by heat was determined in a similar manner. The results are not quite as good as with egg albumen, as it seemed impossible to obtain rates of flow. The results obtained showed the *isoelectric point of this material to be at a PH of 3.9 to 4.2,* depending on the gelatin employed. The experimental results are shown by Tables IV and V.

TABLE IV

ISOELECTRIC POINT OF MATERIAL COAGULATED BY HEAT FROM GELATIN NO. 37

PH	Direction of movement
3.2	Anodic
3.4	Anodic
3.6	Anodic
3.86	Anodic
4.0	Cathodic
4.4	Cathodic
5.4	Cathodic

TABLE V

ISOELECTRIC POINT OF MATERIAL COAGULATED FROM GELATIN NO. 43

PH	Direction of flow of liquid
3.6	Anodic
3.85	Anodic
4.2	Anodic (weak)
4.4	Cathodic (strongly)
4.2 (repeated)	First one way then the other
4.4	Cathodic
5.0	Cathodic

The isoelectric point lies between PH 3.85 and 4.0.

Discussion

The analyses of the material for nitrogen, although not concordant for different gelatins, were in good agreement for the same make. The nitrogen content is in every case much lower than that of gelatin itself (*ca.* 18%) and approaches that of albumins. On the other hand, the total sulfur and labile sulfur contents definitely distinguish it from serum albumin and egg albumen. The lower isoelectric point is in agreement with the lower nitrogen content, although there is no necessity of this following, since it depends, *e. g.,* upon proportion of diamino to monamino acids.

In some properties the material resembles keratose, as described by Wilson, but the low sulfur content is in disagreement with this. More complete analyses are required before the constitution can be established.

Relation to Fractionation of Gelatin.—A so-called "insoluble gelatin fraction" was separated by Knaggs, Manning and Schryver,[8] and their work was extended by Kunitz and Northrop.[9]

The coagulable protein from gelatins appears to be identical with the "insoluble fraction of gelatin" found by Kunitz and Northrop.[9] In their procedure the isoelectric gelatin is dissolved to a 2% solution and kept at a constant temperature of 23° for five or six days. The gelatin solution turns milky, thickens and finally breaks up into clots and precipitates.

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[8] J. Knaggs, A. B. Manning and S. B. Schryver, Biochem. J., 17,473 (1923).

[9] M Kunitz and J. H. Northrop, *J. Gen. Physiol.,* 12, 379 (1929).

After separating the coagulum from the solution it is redissolved and the procedure repeated twelve or fifteen times. A water-insoluble fraction is obtained at the end amounting to only about 1% of the original amount.

A similar substance was obtained by Kunitz and Northrop when they hydrolyzed a 5% solution of gelatin in $M/10$ hydrochloric acid at 90°.

If the "insoluble gelatin fraction" separated by Kunitz and Northrop is actually no constituent of gelatin at all, but a protein impurity, it seems unlikely that it is essential to the swelling mechanism, as suppose by them. We have obtained a gelatin which had merely a trace of this material, but which showed all the usual swelling properties of gelatin, and equal jelly strength and viscosity. We are continuing investigations on this foreign protein and its removal from gelatin.

Summary

It is found that gelatin prepared from calf-skins usually contains a small amount—less than 1%—of a heat coagulable protein as an impurity. The protein approaches albumin (egg albumen and serum) in nitrogen content (around 14%). Its organic sulfur content is considerably higher than that of gelatin (0.8 compared to 0.24%). Its isoelectric point lies at about PH 4.0. It is suggested that the so called "insoluble" gelatin of various investigators is identical with this protein impurity.

ROCHESTER, NEW YORK

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

THE CONSTITUTION OF HOMOMESITYL OXIDE[1]

BY S. G. POWELL AND C. H. SECOY

RECEIVED DECEMBER 1, 1930 PUBLISHED FEBRUARY 9, 1931

The homomesityl oxide derived from 2-butanone has been prepared by numerous investigators.[2] Earlier workers made no attempt to determine its structure, while later investigations produced some evidence that it has the formula $C_2H_5(CH_3)C{=}CHCOC_2H_5$.

Since 2-butanone reacts with aldehydes to give compounds of the type $RCH{=}C(CH_3)COCH_3$, one would expect the structure $C_2H_5(CH_3)C{=}C(CH_3)COCH_3$, and as the evidence in favor of the other formula was not conclusive and involved some contradictions, this investigation was undertaken to determine definitely the constitution of the homomesityl oxide.

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[1] This paper is an abstract of a thesis offered by C. H. Secoy in partial fulfilment of the requirements for the degree of Master of Science in the University of Washington.

[2] (a) Pawlow, *Ann.*, 188, 138 (1877); (b) Schramm, *Ber.*, 16, 1581 (1883); (c) Descudé, *Ann. chim.*, [7] 29, 494 (1903); (d) Rarbier and Leser, Bull. *soc. chim.*, 31, 278 (1904); (e) Bodroux and Taboury, *ibid.*, [4] 3,831 (1908); *ibid*, [4] 5, 950 (1909); (f) Pariselle and Simon, *Compt. rend.*, 173, 86 (1921); (g) Becker and Thorpe, *J. Chem. Soc.*, 121, 1303 (1922); (h) Ekeley and Howe, THIS JOURNAL, 45, 1917 (1923); (i) Franke and Köhler, *Ann.*. 433,314 (1923).

The formula of the homomesityl oxide from 2-butanone was conclusively shown to be $C_2H_5(CH_3)C{=}CHCOC_2H_5$ by hydrogenating it and identifying the resulting octanone as 5-methyl-3-heptanone. Guerbet[3] prepared 5-methyl-3-heptanone and reported the melting point of its semicarbazone as 96°, whereas Bodroux and Taboury reported 102° as the melting point of the semicarbazone of the octanone obtained from homomesityl oxide. As Guerbet's evidence for the structure of his ketone is not very complete, 5-methyl-3-heptanone was prepared by the oxidation of the 5-methyl-3-heptanol obtained by the Grignard synthesis from 1-bromo-2-methylbutane and propionaldehyde. The semicarbazone of this 5-methyl-3-heptanone melted at 96°, as did that of the octanone obtained by hydrogenating homomesityl oxide, contrary to the findings of Bodroux and Taboury. In addition, the properties of the octanol resulting from reduction of homomesityl oxide corresponded with those of the 5-methyl-3-heptanol mentioned above.

As further evidence, the octanone was oxidized and the resulting acids identified as acetic (by conversion to the *p*-bromophenacyl ester) and *sec.*-butylacetic (by comparison of the amide with the amide of known *sec.*-butylacetic acid).

Furthermore, a homomesityl oxide with the structure $C_2H_5(CH_3)C{=}C(CH_3)COCH_3$ would yield on reduction 3,4-dimethyl-2-hexanone. A ketone with this constitution was prepared by the hydrolysis of ethyl *sec.*-butylmethylacetoacetate and was found to differ from the octanone obtained from homomesityl oxide.

Of the previous attempts to determine the structure of homomesityl oxide, that of Becker and Thorpe is the only one that furnished any positive evidence. They treated it with sodio ethyl malonate, hydrolyzed the resulting product to an ethyldimethyldihydroresorcinol and oxidized this to β-ethyl-β-methylglutaric acid, a product which could only arise from a homomesityl oxide with the formula $C_2H_5(CH_3)C{=}CHCOC_2H_5$. Franke and Kohler assumed this structure because they failed to obtain a positive iodoform reaction, which they offer as evidence that the grouping CH_3CO- is absent. In this investigation it was found that chloroform was readily produced by treatment of the homomesityl oxide with sodium hypochlorite and that in the presence of sodium iodide a small quantity of iodoform was also produced. This apparently contradictory evidence is readily explained if preliminary hydrolysis to two molecules of 2-butanone is assumed.

Experimental

Homomesityl Oxide.—This was prepared by a method that is essentially that of Bodroux and Taboury.[4] It was found that more satisfactory results could be obtained

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[3] Guerbet, *Compt. rend.*, 150, 183 (1910).

[4] Bodroux and Taboury, Bull. *soc. chim.*, [4] 3, 831 (1908).

by substituting small muslin bags filled with powdered barium oxide for the lumps of calcium carbide of the original method. In a typical run, 500 g. of 2-butanone yielded 85 g. of homomesityl oxide, b. p. 164–166°, d_4^{21} 0.8633, n_D^{21} 1.4445.

The 2,4-dinitrophenylhydrazone[5] melted at 46°. Chloroform was readily obtained by warning homomesityl oxide with sodium hypochlorite solution, and a small amount of iodoform was produced when sodium hypochlorite solution was slowly added to a well shaken mixture of homomesityl oxide and sodium iodide solution.

Preparation of the Saturated Ketone.—The reduction was carried out as described by Adams and his students,[6] using 0.4 g. of platinum oxide, 31.5 g. (0.25 mole) of homomesityl oxide, and 150 cc. of 95% alcohol. The initial hydrogen pressure was 40 lb.; time of reduction nine minutes; yield of saturated ketone, 94% of the theoretical; b. p. 158°; d_4^{24} 0.829; n_D^{24} 1.412.

The semicarbazone after recrystallization from dilute methanol melted at 96°.

Oxidation of the Saturated Ketone.—Twenty-five grams of the ketone was refluxed for six hours with a mixture of 40 g. of sodium dichromate, 53 g. of sulfuric acid and 200 cc. of water. The whole was then distilled until the residue became quite thick. The distillate was neutralized with sodium hydroxide solution and again distilled until no more unchanged ketone passed over. The residue was acidified and distillation continued, collecting three equal-sized fractions. By refractionation the acids more volatile with steam were concentrated in the first fraction, and the least volatile in fraction 3.

Fraction 1 was extracted several times with ether, the ether solution dried with calcium chloride, the ether removed and the residue distilled. The acid was converted by treatment with thionyl chloride to the acid chloride, which was added drop by drop to concd. aqueous ammonia. The amide which separated on cooling was recrystallized from boiling water and melted at 123°. The amide prepared in the same manner from *sec.*-butylacetic acid (obtained by the ethyl malonate synthesis) also melted at 123°,[7] as did a mixture of the two.

Fraction 3 was neutralized with sodium hydroxide and the solution evaporated to dryness; 0.3 g. of the dry salt was converted into the p-bromophenacyl ester according to the directions of Judefind and Reid.[8] The ester melted at 85° as reported by Judefind and Reid for *p*-bromophenacyl acetate.

Fraction 2, treated in the same manner as fraction 3, proved to contain only acetic acid.

Preparation of the Saturated Alcohol.—Homomesityl oxide was reduced with sodium and moist ether by the method previously described by one of us for the reduction of butylidene ethyl methyl ketone.[9] From 25 g. of homomesityl oxide there was obtained 10 g. of the saturated alcohol boiling at 155°, d_4^{24} 0.8425, n_D^{24} 1.433.

5-Methyl-3-heptanol.—This was prepared by the Grignard synthesis from 36 g. of magnesium, 192 g. of 2-methyl-1-bromobutane, and 100 g. of propionaldehyde. The boiling point, density and refractive index corresponded with those of the saturated alcohol obtained from homomesityl oxide. This is evidently the same alcohol as that obtained by Guerbet[3] by heating 2-butanol with sodium.

5-Methyl-3-heptanone.—Eighteen and one-half grams of 5-methyl-3-heptanol was added drop by drop with constant stirring to a mixture of 15 g. of sodium dichromate, 20

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[5] Allen, THIS JOURNAL, 52, 2955 (1930).

[6] Adams and Voorhees, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, pp. 10, 92.

[7] Van Rombergh, Rec. *trav. chim.*, *6*, 153 (1887).

[8] Judefind and Reid, THIS JOURNAL, 42, 1043 (1920).

[9] Powell, *ibid.*, 46, 2516 (1924).

g. of sulfuric acid and 70 cc. of water, keeping the temperature at about 50°. Stirring was continued for thirty minutes after all of the alcohol had been added, and the mixture then distilled until no more oil passed over. The oil was separated, dried with calcium chloride and distilled. The boiling point, density and refractive index were the same as those of the saturated ketone obtained from homomesityl oxide.

The semicarbazone melted at 96°.

3,4-Dimethyl-2-hexanone.—This was prepared by hydrolyzing ethyl *sec.*-butylmethylacetoacetate by the regular procedure. Ninety grams of ethyl acetoacetate yielded 90 g. of crude ethyl methylacetoacetate, which in turn gave 62 g. of pure ethyl *sec.*-butylmethylacetoacetate. The ketone was obtained by refluxing the ester with 300 cc. of 15% aqueous sodium hydroxide; b. p. 158°, d_4^{22} 0.8295, n_D^{22} 1.412.

The semicarbazone melted at 124–126°.

Summary

1. An improved method for the preparation of homomesityl oxide has been described.
2. The structure of homomesityl oxide is definitely established as $C_2H_5(CH_3)C{=}CHCOC_2H_5$.

SEATTLE, WASHINGTON

[188TH CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE CHEMISTRY OF LIGNIN. V. THE DISTILLATION OF ALKALI LIGNIN WITH ZINC DUST IN AN ATMOSPHERE OF HYDROGEN

BY MAX PHILLIPS

RECEIVED DECEMBER 4, 1930 PUBLISHED FEBRUARY 9, 1931

Considerable difference of opinion prevails among investigators of the chemistry of lignin as to whether this substance belongs to the aliphatic, aromatic, hydroaromatic or heterocyclic series.[1] Among the earliest constitutional formulas for lignin may be mentioned the Keto-R-hexene formula of Cross and Bevan[2] and that proposed by Green.[3]

Willstatter and Kalb,[4] as the result of their work on the reduction of lignin with hydriodic acid and red phosphorus, conclude that lignin is structurally related to the carbohydrates. However, none of the products which they obtained were homogeneous, and they were unable to identify any definite chemical substance.

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[1] An excellent résumé of the literature up to 1926 dealing with the constitution of lignin is given by K. Kiirschner in his monograph, "Zur Chemie der Ligninkörper," p. 141, published in F. B. Ahrens' "Sammlung Chemischer und Chemischtechnischer Vortrage," Vol. 28, Ferd. Enke, Stuttgart, 1926, and in the monograph by W. Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, 1926, p. 277.

[2] Cross and Bevan, "Cellulose," Longmans, Green and Co., London, 2d ed , 1895, p. 137; Vol. III, 1912, p. 104.

[3] Green, *Z. Farben* Textilchemie, 3, 97 (1904).

[4] Willstatter and Kalb, *Ber.*, 55, 2637 (1922).

Jonas[6] and Marcusson[6] contend that lignin is not aromatic but is made up of furan nuclei.

Schrauth[7] assumes that the fundamental unit of the lignin molecule is formed by the condensation of three molecules of 5-hydroxymethylfurfural. The unit so formed consists of a compact condensed ring system, of which three of the outer rings are furan nuclei and the other three outer rings and the central ring benzene nuclei.

The constitutional formulas for lignin, which at various times have been advanced by Klason,[8] all contain at least one aromatic nucleus, generally some coniferyl derivative coupled with a heterocyclic nucleus.

Kürschner,[9] as the result of his investigations on the sublimation of lignin, advanced the hypothesis that lignin is a polymer of the glucoside coniferin. Freudenberg, Belz and Niemann[10] have recently come out in favor of an aromatic structure for lignin. In a more recent publication Freudenberg, Zocher and Dürr[11] advanced the hypothesis that lignin is a condensation product of a-vanillyl-glycerine and a-piperonyl-glycerine.

The present investigation was undertaken with the hope of obtaining degradation products of lignin that would help to clear up even in part the structure of this substance. It was felt that a zinc dust distillation of lignin in an atmosphere of hydrogen might lead to definite degradation products which would throw some light on the chemistry of this compound.

The only work reported in the literature on the zinc dust distillation of lignin is that by Karrer and Bodding-Wiger.[12] They heated lignin with zinc dust at red heat and obtained an oil which they fractionated. None of the fractions were oxygen free, nor did they appear to be homogeneous, nor did these authors identify any definite chemical substance in their distillation product.

In the present investigation three phenolic substances were isolated, two of which were identified as catechol and guaiacol. The third phenol gave a crystalline dinitrobenzoyl derivative melting at 110° and contained the methoxyl group but was not further identified. It was probably a homolog of guaiacol. It is believed that the results obtained in this investigation tend to give support to the hypothesis that at least one aro-

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[5] Jonas, *Wochenbl. Papierfabr.*, **56**, 24A, 83 (1925).

[6] Marcusson, *Z. angew. Chem.*, **34**, 437 (1921); **35**, 165 (1922); **36**, 42 (1923); *Ber.*, **58**, 869 (1925).

[7] Schrauth, *Z. angew. Chem.*, **36**, 149 (1923).

[8] Klason, *Svensk. Kem. Tidskrift*, **1897**, 135; *Arkiv. Kem. Min. Geol.*, **6**, No. 15, 1 (1917); *Ber.*, **53**, 706 (1920); **56**, 300 (1923); **58**, 375, 1761 (1925); **62**, 2523 (1929); **63**, 792, 1548, 1983 (1930).

[9] Kürschner, Ref. 1, p. 164.

[10] Freudenberg, Belz and Niemann, *Ber.*, **62**, 1554 (1929).

[11] Freudenberg, Zocher and Dürr, *ibid.*, **62**, 1814 (1929).

[12] Karrer and Bodding-Wiger, *Helv. Chim. Acta*, **6**, 817 (1923).

matic nucleus exists in the lignin molecule.[13] The presence of other nuclei in addition to the aromatic nucleus is however not excluded.

In all of the experiments, considerable amounts of carbon dioxide were evolved during the distillation. This may be explained on the assumption that lignin contains either a lactone, carboxyl or esterified carboxyl group. Van der Haar[14] has recently shown that only those substances which contain two oxygen atoms attached to the same carbon atom, that is to say, carboxylic acids and their esters and lactones give off carbon dioxide when subjected to a zinc dust distillation in a current of hydrogen. Ketones, aldehydes, alcohols, phenols, quinones, purine derivatives and pyrones do not give off carbon dioxide under these conditions.

Experimental

The apparatus used in these experiments is illustrated in Fig. 1. It consisted of a glass tube, B, 3.5 cm. outside diameter and 45 cm. long. This tube was constricted at one end and bent at a right angle in the form of an adapter. This was attached to a vertical condenser F, to which, in turn, was attached a 300-cc. Erlenmeyer flask, G, the inner tube of the condenser reaching to within about one centimeter of the bottom of this flask. The latter was connected in series to two other 300-cc. Erlenmeyer flasks, G′ and H. Flasks G, G', which served as receivers for the distillate, were immersed in an ice-bath. Flask H contained barium hydroxide solution to collect any carbon dioxide that might come over. The glass tube was inserted into an asbestos-covered metal tube (A) 8.6 cm. in diameter, which served as an air-bath and was held in place by transite end pieces C. This tube was heated by means of three fishtail burners J. The temperature of the bath was determined by means of thermometer D. Dry hydrogen was led into the system through tube E.

The glass tube (B) was filled as follows. A plug of glass wool was placed at the constricted end of the tube. This was followed by a 10-cm. layer of pumice about the size of peas which had been impregnated with zinc dust. The coating of the pumice with zinc dust was accomplished as follows. A paste was prepared by rubbing up 100 g. of zinc dust with 30 cc. of water. The pumice was added to this and the mixture stirred until the pumice was well covered with the zinc dust paste. The pumice was then removed from the paste and dried.

After the pumice–zinc dust layer was placed a mixture consisting of 50 g. of alkali lignin[15] and 150 g. of zinc dust to which had been added some pumice impregnated with zinc dust. Finally a 5-cm. layer of pumice–zinc dust was added.

The distillation experiment was begun by passing through the system a fairly rapid stream of dry hydrogen until all of the air was replaced. The current of gas was then diminished so that only about three bubbles per second passed through. Heat was

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[13] It may be of interest to point out in this connection that phenol ethers had previously been found in the oil obtained by the destructive distillation of lignin (W. Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, 1926, p. 151).

[14] Van der Haar, *Rec. trav. chim.*, 48, 1170 (1929).

[15] The lignin used in these experiments was isolated from corn cobs following the method described in a previous communication [THIS JOURNAL, 51, 2420 (1929)]. It was purified by dissolving in alcoholic sodium hydroxide solution, filtering, distilling off the alcohol and precipitating the lignin with hydrochloric acid. It was washed free from chlorides and dried in *vacuo* at 80°.

then applied under the front and rear ends of the tube containing the layers of pumice–zinc dust. Finally the mixture of lignin and zinc dust was gradually heated until the temperature of the air-bath was 400°. Throughout the experiment the temperature was not permitted to exceed 400°. At first a considerable amount of gas was evolved, including carbon dioxide which was indicated by the barium hydroxide solution first becoming milky and by the subsequent deposition of a precipitate of barium carbonate. Carbon dioxide was given off in all of the experiments.

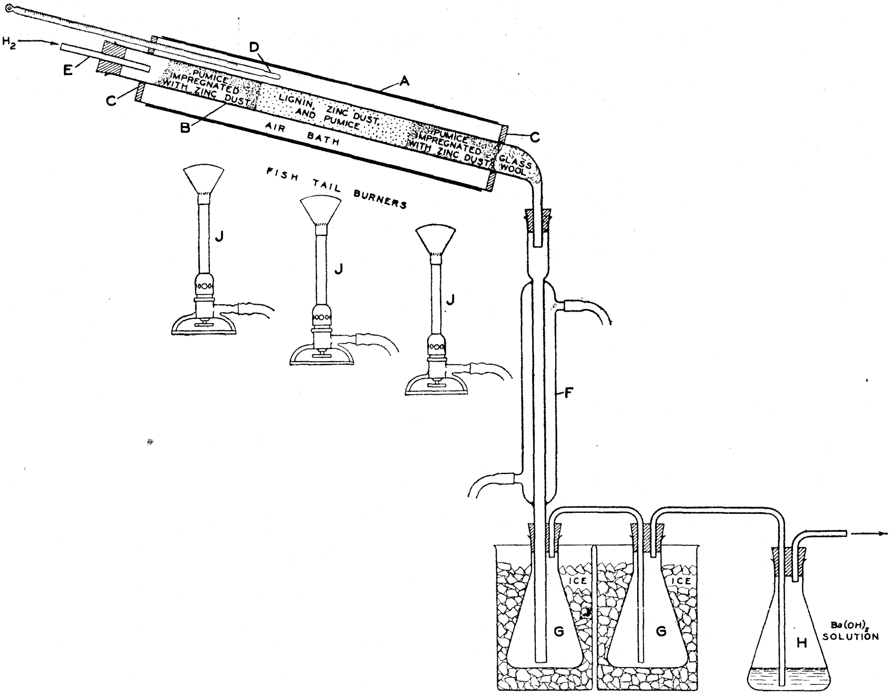

Fig. 1.—Apparatus for distillation of lignin with zinc dust in atmosphere of hydrogen.

Examination of the Distillate.—The distillate consisted of an aqueous portion together with an oil. The combined distillates from five experiments representing a total of 250 g of lignin were combined and worked up. The aqueous portion was separated off, shaken with activated charcoal (Darco) as recommended by Stritar and Zeidler,[16] filtered and the filtrate made up to 500 cc. The oily portion was dissolved in an equal volume of ether, dried over anhydrous sodium sulfate and filtered. Upon removal of the ether by distillation, a brown oil was obtained. The yield was 40 g., equal to 16% of the weight of the lignin used.

Examination of the Aqueous Portion.—The acid in the aqueous distillate was determined by titration with standard alkali and amounted to 0.24% (calculated as acetic acid and on the basis of the weight of lignin used).

The acetone was determined by the Messenger[17] method, which was carried out as

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[16] Stritar and Zeidler, Z. *anal.* Chem., 43, **387** (1904).

[17] Messenger, ***Ber.***. 21, **3366** (1888).

described in a previous communication.[18] The acetone amounted to 0.36% of the weight of the lignin used.

Two 5-cc. samples were analyzed for methanol by the method of Stritar and Zeidler.[16] The weight of silver iodide obtained amounted to 0.1087 g. (mean of two determinations) which corresponds to 1.48% of methanol in the total distillate and equals 0.59% of the weight of lignin used.

The aqueous distillate gave with ferric chloride solution a green coloration which became red on the addition of sodium carbonate. It gave all the other characteristic tests for catechol.[19]

The aqueous distillate gave no test for furfural with aniline acetate paper and none of the tests for ω-hydroxymethylfurfural.[20] Fuchs[21] obtained ω-hydroxymethylfurfural on the distillation of technical pinewood lignin with powdered silver in an atmosphere of carbon dioxide.

Examination of the Oil.—The oil was dissolved in an equal volume of ether and the ether extracted with 5% sodium hydroxide solution. The alkaline extract was then acidified with hydrochloric acid and the oil separated mechanically from the aqueous portion. This was extracted with ether and the phenolic oil previously separated was added to the ether solution. This solution was dried with anhydrous sodium sulfate, filtered and the ether removed by distillation. A dark brown oil was obtained which amounted to 22 g. (equal to 55% of the weight of the original oil). This oil was distilled in a current of steam, and a light yellow oil was obtained which amounted to 11 g. (equal to 27.5% of the weight of the original oil). This oil was first distilled under ordinary pressure and the distillate fractionated under the same pressure. Two fractions were obtained, namely, 200–210" and 210–220°. The amount of each fraction was 4 g. and 3.5 g., respectively. Each fraction gave a greenish color with ferric chloride in alcoholic solution. A portion of fraction 200–210° (1 g.) was added to a solution of 2.3 g. (0.01 mole) of 3,5-dinitrobenzoyl chloride in 20 cc. of pyridine, and the solution heated at its boiling point under the reflux condenser. The solution after cooling was poured into cold dilute sulfuric acid. The yellow and rather viscid substance which separated out was dissolved in ether, the ether solution extracted with 5% sodium hydroxide solution and the ether removed by distillation. A solid crystalline substance was obtained. This was crystallized from 95% ethanol and recrystallized from methanol and ligroin when a substance melting constantly at 141° (corr.) was obtained. The 3,5-dinitrobenzoyl derivative of pure guaiacol was prepared, and the same melting point was obtained. When the two compounds were mixed the resulting mixture was also found to melt at 141°. Fraction 200–210°, therefore, consisted principally of guaiacol. The 3,5-dinitrobenzoyl derivative of a portion of fraction 210–220" was prepared following the method above described. The product, after several recrystallizations from ethanol, methanol and ligroin, melted at 110°. The melting point, however, was not sharp and even after three other recrystallizations it was not possible to obtain a product having a sharp melting point.

Anal. Subs., 0.0800: required 2.50 cc. of 0.2 N acid. Subs., 0.0374: AgI, 0.0223 Found: N. 8.75; OCH_3, 7.88.

The percentages of nitrogen and methoxyl in the dinitrobenzoyl derivatives of guaiacol and creosol are, respectively: N, 8.80, 8.43; OCH_3, 9.74, 9.34. Fraction 210–220° consisted of some undetermined phenol, possibly some homolog of guaiacol.

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[18] Phillips, THIS JOURNAL, 51,2420 (1929).

[19] L. Rosenthaler "Der Nachweis organischer Verbindungen," Ferdinand Enke, Stuttgart, 1923, p. 258.

[20] Ref. 19, p. 147.

[21] Fuchs, Bar., 60, 957 (1927).

The residue in the flask after the steam distillation of the phenols was a black tarry substance and amounted to 4 g. It was distilled under 15 mm. pressure, and practically all distilled over at 150–190°. Nothing definite, however, was obtained from this fraction.

The ether solution of the oil which had been extracted with 5% sodium hydroxide solution was washed with water and then dried with anhydrous sodium sulfate, filtered and the ether removed by distillation. A dark brown oil was obtained. This amounted to 10 g. (equal to 25% of the weight of the original oil). It was distilled under ordinary pressure, whereupon it all distilled over at 200–220°. The distillate was a light yellow oil.

Anal. Subs., 0.1002, 0.1460: CO_2, 0.2770, 0.4027; H_2O, 0.0705, 0.0981. Found: C, 75.38, 75.22; H, 7.87, 7.51. Subs., 0.0774; AgI, 0.0971 = 16.57% OCH_3.

This neutral substance is therefore an ether containing approximately one-half of its oxygen of the form of methoxyl. It did not react with acetic anhydride or benzoyl chloride nor with hydroxylamine or phenylhydrazine. Hydroxyl and carbonyl groups are therefore not present in this substance, and the residual oxygen exists probably in some ring combination.

Estimation of the Amount of Carbon Dioxide Given Off in the Zinc Dust Distillation of Lignin.—Although van der Haar[13] in applying the zinc dust distillation method for the quantitative determination of carboxyl groups has shown that the method invariably gives low results, it seemed nevertheless of interest to determine the approximate amount of carbon dioxide given off it? the zinc dust distillation of lignin. Accordingly, three experiments were conducted in which 5 g. of lignin and 50 g. of zinc dust were used in each case. The distillation was conducted with the apparatus and under the experimental conditions previously described. The carbon dioxide given off was absorbed in a barium hydroxide solution contained in flask H (Fig. 1). The barium carbonate formed was filtered off and washed with water, free from carbon dioxide, until the wash water was no longer alkaline. The carbonate was dissolved in warm dilute hydrochloric acid and the barium determined as the sulfate. From the weight of barium sulfate obtained the quantity of carbon dioxide was calculated. The results obtained were as follows:

$BaSO_4$, g.	CO_2, g. (calcd. from $BaSO_4$)
1.0756	0.2027
1.0520	.1983
1.0807	.2037

Mean 0.2015 $\approx$ 0.2060 g.–COOH = 4.12%

Assuming that the composition of corn cob lignin may be represented by the formula $C_{40}H_{46}O_{16}$[22] and on the basis of one carboxyl group, the calculated value is 5.75% of COOH.

Summary

1. Alkali lignin, isolated from corn cobs, was distilled with zinc dust in an atmosphere of hydrogen. The distillate consisted of an aqueous portion and an oil. The aqueous distillate contained methanol, acetone and an acid (determined as acetic acid) to the extent of 1.48, 0.36 and 0.24%, respectively (calculated on the basis of the weight of lignin used). Catechol was shown to be present in the aqueous distillate. The yield of

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[22] Phillips, THIS JOURNAL, 49,2037 (1927).

oil obtained amounted to 16% of the weight of the lignin used. Fifty-five per cent. of the oil was alkali-soluble, and in this fraction guaiacol was definitely identified. A phenol containing the methoxyl group and yielding a 3,5-dinitrobenzoyl derivative melting at 110° was also obtained but was not further identified.

2. The isolation of catechol and guaiacol as degradation products of lignin is believed to lend support to the hypothesis that lignin contains an aromatic nucleus.

3. The evolution of carbon dioxide in the zinc dust distillation of lignin in an atmosphere of hydrogen indicates that, in all probability, the lignin molecule contains at least one carbon atom directly united to two oxygen atoms. This may indicate the presence of either a carboxyl group, free or esterified, or a lactone group in the lignin molecule.

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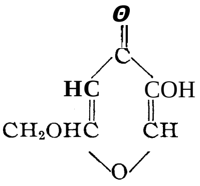
[185TH CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE PRODUCTION OF KOJIC ACID BY ASPERGILLUS FLAVUS

BY O. E. MAY, A. J. MOYER, P. A. WELLS AND H. T. HERRICK

RECEIVED DECEMBER 5, 1930 PUBLISHED FEBRUARY 9, 1931

In the course of a survey of the action of a number of fungi on solutions of xylose and dextrose it was observed that the culture liquors from a strain of *A. flavus* on both sugars gave a deep red coloration upon the addition of ferric chloride solution. Continuous extraction of these cultures with ether yielded a quantity of material crystallizing as colorless needles, soluble in water, methanol, ethanol and ethyl acetate. It was identified as kojic acid by its melting point (152.6' (corr.); Yabuta, 152°; Mauer, 152°; Kinoshita, 154°), by the melting point of the mono-bromo derivative (161° (corr.); Yabuta, 159–160°), and by analysis of the insoluble copper salt (found, average of six determinations, 22.40% CuO. Calcd. for $Cu(C_6H_5O_4)_2\cdot{}^1/_2H_2O$, 22.44%; Mauer found 22.12% CuO). The crystalline products obtained from the xylose and dextrose solutions were identical in all their properties.



Kojic acid was first isolated by Saito[1] from mycelia of *A. oryzae* which had been cultured on steamed rice. He thought it to be identical with β-resorcylcarboxylic acid. Shortly thereafter Yabuta[2] undertook an extensive investigation of the substance, gave it the name kojic acid and.

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[1] K. Saito, *Botan. Mag.* (Japan), 21,249 (1907)

[2] T. Yabuta, *J. Coll. Agr*, *Tokyo,* 5, 51 (1912); *8th Int. Cong. Applied Chem., Appendix,* 25, 455 (1912); *J. Chem. Soc. Japan,* 37, 1185 (1916) (in Japanese); see *Chem. Abs.,* 17, 1475 (1923); J *Chem. Soc.,* 125,575 (1924).

finally, in 1924, definitely established its constitution. Traetta-Mosca reported the formation of the same compound by A. *glaucus* from sucrose, levulose, dextrose and glycerol and also noted that it was fermented to ethanol by yeast.[3] Wijkman, using an unnamed strain of Aspergillus and employing quartz or paraffined glass vessels as culture flasks, consistently obtained the acid from sucrose.[4] Kinoshita has observed that a deficiency in the supply of nutrient nitrogen resulting from the use of cobalt ammines as nitrogen sources caused an increased production of kojic acid by a strain of A. oryzae. Thus, when cobalt purpureo chloride in a concentration of 0.5% was used as the source of nutrient nitrogen, 33% yields by weight were obtained from 10% sucrose solutions in twenty-five days.[5] Tamiya found that a P_H of 5.5 was most favorable to the formation of the acid by *A.* oryzae and later reported the production of the compound from sucrose by the following Aspergilli: oryzae, *flavus* var., *gymnosardae*, *awamori*, *candidus*, *clavatus*, fumigatus and *giganteus*.[6] Challenger, Klein and Walker pointed out that, from the standpoint of molecular structure, since dextrose yields kojic acid, arabinose might by analogy be expected to give rise to pyromeconic acid. To test this hypothesis, they cultured a strain of A. oryzae on solutions of highly purified arabinose and xylose. Kojic acid was the only pyrone compound found in the culture liquors. Moreover, they recovered it from the pentose cultures in yields of the same order of magnitude as those obtained from dextrose.[7] Katagiri and Kitahara found the optimum conditions for the formation of kojic acid by *A.* oryzae to be in 5% dextrose solutions containing 0.05% ammonium sulfate, at P_H 2.4.[8] Corbellini and Gregorini made a study of the formation of the acid from various carbon sources by different strains of A. *flavus* and concluded that the pyrone nucleus was synthesized from substances containing a chain of three carbon atoms resulting from the fragmentation of larger molecules such as the pentoses and hexoses.[9] Starting with acetobromoglucose, Mauer has recently succeeded in synthesizing kojic acid, confirming the structure established for the natural product by Yabuta.[10]

Continuous extraction with ether of a ten-day culture of *A. flavus* No. 3538 on 15% solutions of commercial dextrose yielded 22.69 g. of pure kojic acid per 100 g. of pure dextrose originally present in the culture solution. The comparatively high yield obtained in this short period of culture led

[3] F. Traetta-Mosca, *Ann. chim. appl*, 1, 4777 (1914); F. Traetta-Mosca and M. Preti, *Gazz. chim. ital.*, 51, 269 (1921).

[4] N. Wijkman, *Z. physiol. Chem.*, 132, 104 (1924).

[5] K. Kinoshita, *Acta Phytochimica*, 3, 31 (1927).

[6] H. Tamiya, *ibid.*, **3**, 51 (1927). H. Tamiya and T. Hida, *ibid.*, 4, 343 (1929).

[7] F. Challenger, L. Klein and T. K. Walker, *J. Chem. Soc.*, 1498 (1929).

[8] H. Katagiri and K Kitahara, *Bull. Agr. Chem. Soc. Japan*, 5, 38 (1929)

[9] A. Corbellini and B. Gregorini, *Gazz. chim. ital.*, 60, 244 (1930).

[10] K. Mauer, *Ber.*, **63**, 25 (1930).

to an investigation of some of the more important variables affecting the fermentation, such as nutrient salts, temperature and concentration of dextrose, with a view to increasing the yields to a point which would make **the** process of industrial interest and stimulate a search for uses for this hitherto unavailable pyrone.

Experimental

The organism (No. **3538)** was secured from the collection of Dr. Charles Thom, where it had been kept in continuous culture since 1914. Its appearance was typical of the *flavus–oryzae* group and its mycological characteristics are to be described in a forthcoming publication.

For the most part, the experiments were carried out in 200-cc. pyrex glass Erlenmeyer flasks as culture flasks. The dextrose was of commercial grade and contained approximately 91.5% dextrose, 8.0% water, 0.5% dextrin and other non-reducing carbohydrates. Nutrient salts were added in the following concentrations, except when stated otherwise.

	G./liter of dextrose solution
$MgSO_4{\cdot}7H_2O$	0.500
KCl	.100
H_3PO_4	.054
NH_4NO_3	1.125

Seventy-five cc. of culture solution per flask was used to give a surface area/volume ratio of approximately 0.4. The solutions were sterilized for fifteen minutes at 15 lb. steam pressure and after cooling were inoculated with spores of the organism. All cultures were run in duplicate or triplicate.

At the conclusion of the fermentation the contents of the culture flask were heated and filtered with suction through a weighed filter paper. The mycelium was thoroughly washed with three 25-cc. portions of hot distilled water, the washings were added to the culture liquors and the volume of the combined solutions was noted. The filter paper and mycelium were placed in a tarred weighing bottle, dried at 90° for two days and the weight of the dry mat was obtained. Reducing sugar, calculated as dextrose, was determined by the Shaffer–Hartman method, using the citrate–carbonate reagent. In the presence of kojic acid it was impossible to determine the true end-point in the thiosulfate titration when starch was used as the indicator because of the difficulty in discharging the starch–iodine color. For this reason starch was not used, and the typical sharp color change from green to blue was utilized to indicate the disappearance of the iodine. However, in experiments where the concentration of kojic acid exceeded **3** g. per 100 cc. of solution, control titrations indicated that a true end-point was not obtained. In such cases it was necessary to dilute the sample so that the above-mentioned concentration of acid was not exceeded or, where the concentration of sugar was low, to remove the acid as the insoluble copper salt and make the determination on the filtrate. Since kojic acid reduces hot alkaline copper solution, a correction, determined by the quantity of acid present, was applied to the values obtained for reducing sugars. The reduction values of kojic acid in terms of mg. of copper were determined and are given in Table I.

TABLE I

KOJIC ACID REDUCTION VALUES

Kojic acid, mg.	5	10	20	30
Cu, mg.	9.5,	17.0,	35.0,	52.0

The acid was determined by neutralization of an aliquot of the culture liquors with dilute alkali and precipitation of the partially hydrated copper salt with $N/10$ cupric acetate. The precipitate was dried at 100°, weighed and the acid calculated on the basis of $Cu(C_6H_5O_4)_2 \cdot {}^1/_2H_2O$. In the absence of other acids, kojic acid can be estimated accurately by titration with dilute alkali, with alizarin orange R as the indicator. However, in our experiments the culture solutions were invariably colored a deep yellow, which interfered somewhat with the observation of the color change of the indicator.

The yields were calculated as the ratio of the dextrose required to give the quantity of kojic acid formed to the total dextrose originally present in the culture solution.

At the outset of these experiments it became apparent that the source of nutrient nitrogen was of prime importance among the factors governing the formation of kojic acid. The effect on acid production of some nitrogen-containing salts is shown in Table II. Ammonium sulfate was unsatisfactory, and it is of interest that its use almost completely suppressed sporulation. Ammonium nitrate was most satisfactory. The effect of variation in its concentration is given in Table III. Nitrates, while supporting a vigorous vegetative development, were found to have an adverse effect on acid formation when used in conjunction with the standard salt

TABLE II

EFFECT OF SOURCE OF NUTRIENT NITROGEN

Temperature, 22°; duration of culture. 14 days; concentration of commercial dextrose, 15%; volume, 75 cc.

N source	G. N/liter	Yield of kojic acid G.	Yield of kojic acid %	Mycelium, g.
$(NH_4)_2SO_4$	0.70	0.90	10.0	0.320
$(NH_4)_2SO_4$	1.75	1.04	11.7	.342
$(NH_4)_2HPO_4$	0.70	1.45	16.3	.526
$(NH_4)_2HPO_4$	1.75	1.65	18.6	.558
NH_4NO_3	0.70	1.66	18.6	.432
NH_4NO_3	1 75	1.45	16.3	.461
$NaNO_3$	0.70	0 08	1.0	.277

Table III

Effect of Variation in Concentration of Ammonium Nitrate

Temperature, 25°; **duration of culture,** 13 **days; concentration of commercial dextrose.** 15%; **volume,** 75 **cc.**

NH_4NO_3, g./liter	Yield of kojic acid G.	%	Sugar consumed, g.	Yield of kojic acid, based on sugar consumed, %	Mycelium, g.
0.142	0.430	4.8	1.4	39.0	0.124
.281	2.48	27.9	5.5	57.2	.146
.563	2.69	30.2	6.4	53.2	.204
.750	2.65	29.8	7.2	46.7	.235
1.125	2.61	29.4	6.7	49.4	.282
2.250	2.40	27.0	6.1	49.9	.261
4.500	2.03	22.8	**Undetermined**	..	.245

solution, as noted in Table II, but when type and concentration of the added salts were changed, a decided increase in the quantity of kojic acid produced was noted, as will be observed in Table IV. That this increase was not due to the direct nutritive value or to physical effects of these added salts is evident from the results with ammonium nitrate, where a slightly lower yield was obtained than in experiments where the standard salt solution was used. With both nitrates and ammonium salts, however, in all cases the use of the B solution induced an appreciably greater vegetative development.

Temperature was found to have a decided effect on the quantity of kojic

Table IV

Comparison of Ammonium Nitrate and Sodium Nitrate Used with Two Nutrient Salt Solutions

Temperature, 30°; **duration of culture,** 12 **days; commercial dextrose,** 20%; **culture** vol., 75 **cc.**

A—Salts (KCl 0.1, H_3PO_4 0.054, $MgSO_4 \cdot 7H_2O$ 0.5 g./liter.)
B—Salts (KH_2PO_4 1.0 **and** $MgSO_4 \cdot 7H_2O$ 2.0 g./liter.)

Solutions, nitrogen source, g./liter	Yield of kojic acid G.	%	Sugar consumed, g.	Yield of kojic acid, based on sugar consumed, %	Mycelium, g.
		Sodium Nitrate			
A—0.62	0.13	1.2	2.2	7.5	0.298
B— .62	.19	1.8	2.0	12.1	.351
A —1.66	.35	3.2	3.0	14.8	.503
B—1.66	2.56	23.7	8.8	36.9	.750
A—5.00	0.35	3.2	3.2	13.9	.514
B—5.00	2.19	20.5	12.0	23.3.	1.281
		Ammonium Nitrate			
A—0.28	2.49	23.0	6.3	50.0	0.180
B— .28	2.23	21.2	6.0	47.1	.222
A— .75	3.69	34.2	8.0	58.5	.223
B— .75	3.10	28.7	9.3	42.3	.312
A—2.25	4.83	44.7	10.0	61.1	.317
B—2.25	4.72	43.7	12.1	49.5	.511

acid produced. A range from 30 to 35° promoted rapid vegetative development with high yields of acid as shown in Table V. Respiration was apparently much accelerated at the high temperature.

In a range of sugar concentrations from 15 to 33%, inclusive, growth and acid production were satisfactory, the highest yield, based on the sugar originally present, occurring at a concentration of 20%. It is worth noting that the yields obtained in four different concentrations are practically the same when calculated on the basis of sugar consumed. With concentrations above 40% osmotic pressure apparently had an unfavorable effect, since the production of acid dropped off sharply, as indicated in Table VI.

TABLE V

EFFECT OF TEMPERATURE

Duration of culture, 12 days; concentration of commercial dextrose, 15%; volume, 75 cc.

Temp., °C.	Yield of kojic acid G.	%	Sugar consumed, g.	Yield of kojic acid, based on sugar consumed, %	Mycelium, g.
22	1.82	20.5	4.3	53.6	0.255
25	2.40	27.0	5.2	58.5	.260
30	4.00	45.0	8.1	62.6	.333
35	4.05	45.5	10.0	51.4	.370

Several experiments were carried out in which the depth of the culture medium was varied in solutions of the same sugar concentration. Some representative results are given in Table VII. As in most mold fermentations of this type, the ratio of the surface area of the mycelium to the

TABLE VI

EFFECT OF CONCENTRATION OF DEXTROSE

Duration of culture, 12 days; temperature, 35°; volume, 75 cc.

Commercial dextrose, %	Yield of kojic acid G.	%	Sugar consumed, g.	Yield of kojic acid, based on sugar consumed, %	Mycelium, g.
10	0.37	4.1	5.8	8.1	0.856
15	4.05	45.5	10.0	51.4	.370
20	5.20	48.2	12.8	51.6	.375
22.2	4.82	40.8	12.0	51.0	.373
33.3	4.65	26.2	11.5	51.3	.297
44.4	2.70	11.4	10.0	34.3	.221

TABLE VII

INFLUENCE OF CULTURE MEDIUM DEPTH

Temperature, 24–25'; concentration of commercial dextrose, 22%

Vol. of medium, cc.	Depth of medium, cm.	Surface area/vol.	Kojic acid formed in 7 days, g.	Duration of culture, days	Yield of kojic acid G.	%	Est. time for 40% yield, days
333.0	1.4	1.00	14.1	12	30.5	57.5	9
666.0	2.5	0.50	17.9	14	44.0	42.9	13
1000.0	3.5	.30	17.7	17	68.2	43.3	16
1333.0	5.8	.22	11.3	25	92.6	44.1	22

volume of the solution governs, to a large extent, the yields obtained, especially in shorter periods of culture. The maximum quantities of acid were most economically produced in 12-day cultures when this ratio had a value of from 0.3 to 0.5.

The rates of acid production, sugar consumption and vegetative growth on 20% solutions at 35° are given by the curves in Fig. 1. As soon as the supply of sugar is exhausted, the acid is utilized by the organism and slowly disappears with a corresponding diminution in the weight of the mycelium. Whether the decrease in mass of the mycelium is due to a slow autolysis cannot be definitely stated.

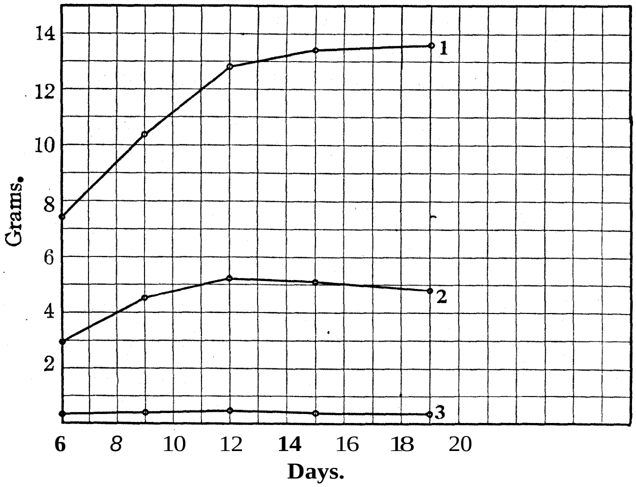

Fig. 1.—1, Sugar consumed; 2, kojic acid produced; 3, dry weight of mycelium.

The formation of this hydroxy pyrone by fungi from carbohydrates in large quantities in a short period of time is a striking phenomenon considering the relatively small quantities of related compounds found in the higher plants. Thus chelidonic acid (2,6-dicarboxy-1,4-pyrone) occurs in the leaves of lily of the valley to the extent of 2% and meconic acid (2,6-dicarboxy-3-hydroxy-1,4-pyrone) is found in opium to the extent of approximately 4%, while maltol (3-hydroxy-2-methyl-1,4-pyrone) is a minor constituent of pine needles and the bark of larches. The fact that pyrones in general react readily with ammonia to form pyridones may have an important bearing on the problem of the origin of pyridine bases found in plants, and the widespread occurrence of flavone compounds in the plant kingdom further emphasizes the importance of the pyrone nucleus in nature. Hence a detailed study of the mechanism of kojic acid formation might throw considerable light on the complete obscurity surrounding the mode of formation of these related substances in the plant cell.

Yabuta[2] thought that the formation of the acid by *A. oryzae* was connected in some manner with the oxidation changes brought about in the reduction of hexoses to the corresponding alcohols, but Kinoshita[5] pointed out that this was not necessarily so, since the organism formed kojic acid when mannitol was used as the sole carbon source. Owing to its close structural relationship to dextrose, Haworth has suggested that kojic acid resulted from the oxidation and dehydration of that hexose,[11] but the yield of acid obtained by Challenger, Klein and Walker from xylose and arabinose, as well as the fact that it is formed when levulose is used as the carbon source, casts doubt on such a mechanism. Moreover, kojic acid has been reported as being produced by Aspergilli from the following additional compounds: starch, inulin, sorbitol, dulcitol, sucrose, mannose, galactose, glycerol, glycero-&phosphate and gluconic acid. Corbellini and Gregorini[9] believe that the pyrone nucleus is synthesized from molecules containing three carbon atoms by a reaction analogous to that brought about by the enzyme carboligase of yeast. They suggest that glyceraldehyde condenses with a molecule of another oxidation product of glycerol to give a product which by dehydration goes over to kojic acid.

The ready formation of pyrone compounds through the dehydration of appropriate acyclic polyketones is well known. Thus dimethylpyrone is formed from diacetylacetone through simple and even spontaneous loss of water at ordinary temperatures and likewise the dehydration of acetonedioxalic acid gives rise to chelidonic acid. If an analogous reaction were postulated as the final step in the formation of kojic acid, the immediate precursor of this hydroxypyrone would be 1-hydroxyacetyl-3-formyl-3-hydroxyacetone ($CH_2OHCOCH_2COCHOHCHO$). Whether this compound could result from reactive oxidation products of either methylglyoxal, glyceraldehyde or acetaldehyde is not known. The results obtained up to the present point to a synthesis of kojic acid from some reactive substance, as yet not isolated, containing two or three carbon atoms, and evidence is slowly accumulating that definitely indicates the production by fungi of such compounds of low molecular weight. The formation of acetaldehyde in the metabolism of several molds has been demonstrated,[12] but its biological significance is not yet clear. As a result of a study of this aldehyde in the citric acid fermentation induced by *A. niger,* Bernhauer concluded that there was no relation between it and the formation of the acid, as the quantity of acetaldehyde produced was entirely too small.[13] Nevertheless, the biological formation of citric acid from widely different carbon sources seems to indicate a distinct synthetic reaction. Yuill has

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[11] W. Haworth, "Constitution of Sugars," London, 1929, p. 38.

[12] C. Cohen, *Biochem Z.,* 112, 139 (1920); C. Neuberg and C. Cohen, *ibid.,* 122, 204 (1921).

[13] K. Bernhauer, *ibid.,* 202, 169 (1928).

reported the formation of appreciable quantities of ethanol but no kojic acid by a strain of *A. flavus* cultured on sucrose solution in the usual manner,'* and the recent work of Butkewitsch and Fedoroff has established the importance of ethanol and acetic acid as intermediate substances in the reactions leading to the formation of succinic and fumaric acids by *Mucor stolonifer.*[15] From the fact that in his experiments identical fats were produced from dextrose and xylose by a strain of *Penicillium,* Barber concluded that these sugars are broken down by the organism into smaller molecules from which the fats are then synthesized.[16] It is worth noting, moreover, that up to the present no organism has been found which produces citric or kojic acids from four or seven carbon sugars or sugar alcohols. It is entirely possible that there is a single reactive substance formed by these organisms through the degradation of sugars and other carbon sources which is the starting point for the synthetic reactions brought about through their agency. Whether this substance is acetaldehyde, which serves so well in accounting for the products of yeast and bacterial fermentations, or a closely related compound, remains to be established.

Summary

The effects of variation in nutrient nitrogen, temperature, concentration of sugar and depth of culture solution on the production of kojic acid by *A. flavus* have been investigated. With 20% dextrose solutions, this organism, under favorable conditions, was found to be capable of transforming more than 45% of the dextrose present and 55% of that consumed into kojic acid in twelve days from the time of inoculation from spores.

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[14] *J. Yuill, Biochem. J.,* 22, 1504 (1928).

[15] W. **Butkewitsch** *and M. Fedoroff, Biochem. Z.,* **219,** 87, **103 (1930).**

[16] **H. Barber,** *Biochem. J.,* 23, 1158 **(1929).**

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF OREGON]

THE FURTHER FRACTIONATION OF YEAST NUTRILITES AND THEIR RELATIONSHIP TO VITAMIN B AND WILDIERS' "BIOS"

BY ROGER J. WILLIAMS AND ELIZABETH M. BRADWAY

RECEIVED DECEMBER 8, 1930 PUBLISHED FEBRUARY 9, 1931

Different so-called strains of *Saccharomyces cerevisiae* have diverse requirements for their growth stimulation as is evidenced by the contradictory results of many workers[1] and the experimental study made in this Laboratory.[2] In this publication it was reported that yeast of the type "Gebriide Mayer" (wholly unlike several others) is stimulated almost as effectively by extracts which have been shaken with fuller's earth as by untreated extracts. Similar results had been obtained previously on yeast autolysate by Eddy, Kerr and Williams,[3] when they cultured "Gebriide Mayer" yeast.

We have tried numerous means to purify this yeast nutrilite which is not adsorbed by fuller's earth, but with only moderate success. No adsorbent has been found which will remove it from solution effectively and not one of the numerous precipitants tried, precipitates the substance in question satisfactorily. The most potent preparations obtained by us were made by using various adsorbents and precipitants in sequence and in each case rejecting the precipitated or adsorbed material We have thus obtained material approximately ten times as potent as the original material which was extracted directly from rice polish. Experimental details regarding this work will not be presented at this time because we feel that our efforts have been rewarded with comparatively little success and it will be better to wait until we have made further progress on the problem.

On several occasions we tested preparations to ascertain whether we had separated two factors which might be ineffective when introduced singly but which might supplement each other. We have no indications that this is the case and so far as present evidence is concerned the yeast nutrilite which stimulates the growth of Gebriide Mayer yeast may be a single substance. Our results on this are in agreement with those of Eddy and his co-workers[3,4] who have worked with Gebriide Mayer yeast and have never reported a supplementary action between their preparations. Peskett and O'Brien,[5] who are probably working with this same (baker's)

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[1] It is not appreciated by all investigators in this field that commercial yeast propagation is not necessarily a fixed and immutable process, and that improved strains of yeast may be introduced from time to time. Hence the term "bakers' yeast," for example, does not have a definite meaning when used in connection with these studies.

[2] R. J. Williams, M. E. Warner and R. R. Roehm, THIS JOURNAL, 51, 2764 (1929).

[3] W. H. Eddy, R. W. Kerr and R. R. Williams, *ibid.*, 46, 2846 (1924).

[4] R. W. Kerr, *Proc. Soc. Expt. Biol. Med.*, 25, 344 (1928).

[5] G. W. Peskett and J. R. O'Brien, *Chemistry Industry*, June 20, 1930.

yeast, have found no evidence that their "bios" is a complex. Narayanan,[6] who has studied a yeast presumably of the same type, says "No evidence to support the complex nature of 'bios' has been obtained."

The description of "bios" originally given by Wildiers was that of a substance which was not precipitated by any of the ordinary precipitants. In fact its properties seemed to be very much like those of the nutrilite which stimulates Gebriide Mayer yeast. We thought it worth while to study further the question as to the identity of the Gebriide Mayer nutrilite and the "bios" of Wildiers. For this purpose we were fortunate in obtaining from Professor M. Ide of Louvain, Belgium, a culture of the yeast with which Wildiers' original work was done. The yeast culture as received was labeled Strain of *Sacch.* Cerev. *1* Hansen, Saccharomyces *Wildiersii.* For convenience we shall refer to this as Wildiers' yeast.

Wildiers' yeast, like Gebriide Mayer, is stimulated nearly as well by yeast extracts which have been treated with fullers' earth as by untreated extracts. This is shown by the results given in Table I. The tests were carried out and the determinations of yeast crops made in accordance with the technique outlined in previous publications[2,7,8] from this Laboratory. The yeast extract was prepared by extracting dry yeast with eight times its weight of hot 60% methanol, evaporating the filtrate to dryness and making up to one-half of its original volume with water. Its PH was adjusted to about 5, and a 50-cc. portion was shaken for ten minutes with 2.5 g. of fuller's earth and filtered.

TABLE I

TREATMENT OF EXTRACTS WITH FULLER'S EARTH (WILDIERS' YEAST)

Addition to synthetic medium (10 cc.)		Galvanometer deflection	Yeast crop, mg., dry wt.
1 cc. H_2O		34.5	0.43
1 cc. H_2O		35.45	.38
Untreated extracts from	5 mg. of yeast	32.8	.58
	5 mg. of yeast	33.35	.54
	10 mg. of yeast	29.6	.91
	10 mg. of yeast	30.65	.81
	20 mg. of yeast	25.2	1.38
	20 mg. of yeast	24.55	1.47
Same extracts treated with fuller's earth	5 mg. of yeast	32.35	0.64
	5 mg. of yeast	33.3	.54
	10 mg. of yeast	31.2	.74
	10 mg. of yeast	31.0	.75
	20 mg. of yeast	27.45	1.14
	20 mg. of yeast	27.4	1.13

Original total seeding about 1,400,000 cells.

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[6] Narayanan, ***Biochem. J.***, 24, 6 (1930).

[7] R. J. Williams and R. R. Roehm, **J. *Biol.* Chem.,** 87,581 (1930).

[8] R. J. Williams, E. D. McAlister and R. R. Boehm, *ibid.*, 83, 315 (1929).

In this and other experiments which are not reported in detail, some activity is removed by fuller's earth treatment and by the use of a sufficient amount of fuller's earth a considerable amount of activity may be removed. However, we have no evidence that the nutrilite which functions for Wildiers' yeast is any different from that which stimulates the growth of Gebrüde Mayer yeast. While we have had some slight indications in this direction, we must say that we have no proof either from our work or that of others that Wildiers' "bios" is other than a single substance. While preparations made in different ways aid in the stimulation of this yeast, evidence as to a supplementary relationship between them is largely lacking. Later experiments may prove that Wildiers' "bios" is multiple in nature.

We have what seems to be conclusive evidence that the yeast growth stimulants, with which W. Lash Miller[9,10] and his associates in Toronto have been working, are entirely different from Wildiers' "bios." Through the kindness of Dr. Miller we have been furnished with a culture of the yeast with which his experiments have been carried out.

We have been able to show that unlike any other of the seven representative yeasts tested in our laboratory, W. L. Miller's yeast is stimulated in its growth to an appreciable extent by highly purified inositol. In this respect Miller's yeast behaves entirely unlike Wildiers' yeast, as is shown in Table II. This is one of two separate experiments which gave similar results. It will be noted that our method of testing shows a very definite response on the part of Miller's yeast to inositol alone when as much as 1 mg. is added to 12 *cc.* of medium. This response is definitely lacking in the case of Wildiers' yeast.

TABLE II

EFFECT OF INOSITOL ON W. L. MILLER'S AND WILDIERS' YEASTS

Addition to synthetic medium	W. L. Miller's yeast Galv. reading	W. L. Miller's yeast Mg. of yeast	Wildiers' yeast Galv. reading	Wildiers' yeast Mg. of yeast
1 cc. of H_2O	31.25	0.74	35.35	0.38
1 cc. of H_2O	31.85	.69	36.6	.27
1 mg. of inositol in 1 cc. of H_2O	23.7	1.59	36.7	.27
1 mg. of inositol in 1 cc. of H_2O	24.05	1.55	36.9	.26
Seeding, cells	1,300,000		1,600,000	

Even more striking evidence that the nutrilites for Miller's yeast are quite different from Wildiers' "bios" is based upon the effects of tea extracts on these two yeasts. We find, in confirmation of the work of Miller and Eastcott, that tea is a good source of the nutrilites for Miller's yeast. For this purpose our sample of tea was about the equivalent of our rice polish. However, for Wildiers' yeast and all of the other yeasts which we

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[9] W. L. Miller, Science, 59, 197 (1924).

[10] E. V. Eastcott, *J. Phys. Chem.*, 32, 1094 (1928).

have tested, the rice polish was much richer than the tea. The contrast between these two materials is especially striking in the case of Wildiers' yeast, as is shown in Table III. In one experiment which is not reported in detail tea was distinctly superior to rice polish as a source of nutrilites for Miller's yeast. It seems fair to conclude that the growth-stimulating substances which are abundant in tea are quite distinct from Wildiers' "bios," since they do not stimulate Wildiers' yeast. This conclusion is in line with the fact that Miller and his co-workers have repeatedly and without difficulty fractionated their material into supplementary fractions, whereas attempts on our part to do so with the nutrilite which is effective for Wildiers' yeast have failed repeatedly to yield any such results.

TABLE III

EFFECTS OF RICE POLISH AND TEA EXTRACTS ON W. L. MILLER'S AND WILDIERS' YEASTS

	Yeast crop W. L. Miller's yeast			Yeast crop Wildiers' yeast		
Addition to synthetic medium	Galv. deflection	Mg. of dry yeast	A over blank	Galv. deflection	Mg. of dry yeast	A over blank
1 cc. of H_2O	31.05	0.77	..	34.8	0.40	..
Ext. of 5 mg. of rice polish	23.55	1.60	0.83	29.2	0.95	0.45
Ext. of 10 mg. of rice polish	19.15	**2.22**	1.45	23.95	1.56	1.16
Ext. of 5 mg. of tea	23 5	1.61	0.84	34.45	0.44	0.04
Ext. of 10 mg. of tea	20.7	1.99	1.22	33.65	.51	.11
Seeding	1,200,000 cells			1,550,000 cells		

It appears, therefore, that Miller and his associates should be credited with the discovery of a new series of yeast nutrilites, at least one of which is abundant in tea. These appear to be entirely distinct so far as present evidence indicates from the "bios" described by Wildiers.

The requirements (for growth stimulation) of old process bakers' yeast (with which the senior author's first experiments were carried out), yeast 578 of the American Type Culture collection and Untergarige Hefe K, seem to be more complex than those of Wildiers' yeast. They can readily be resolved into a number of interdependent growth stimulants of which the "bios" of Wildiers may be one, since one of the factors appears to have properties and occurrences similar to those of Wildiers' "bios."

The growth stimulants for the yeasts listed above appear to be different from those concerned in the growth stimulation of Miller's yeast, since these yeasts are not affected appreciably by inositol and we have been unsuccessful in fractionating the nutrilites by the same means used in the Toronto laboratories.

Our work on these yeasts has recently been concerned largely with yeast 578, partly because a considerable amount of work was done with it when the old process culture was not available and partly because it seems to give relatively regular and reproducible results.

Previous work published in 1927[11] has shown that yeast 378 xequires for growth stimulation two substances (or groups of substances) which can be separated by, adsorption of fuller's earth and which have little effect when introduced into the medium singly. More recently[12] it was shown that the crystalline antineuritic vitamin as prepared by Jansen and Donath is extremely potent as a yeast growth stimulant when used in conjunction with the residue of a yeast extract which is not adsorbed by fuller's earth. It was also shown, however, that the antineuritic vitamin of Jansen and Donath is not the only substance which can function in this manner.

Previous publications from this Laboratory have shown, therefore, that for the stimulation of the growth of yeast 578 (and old process yeast) there is required (1) material not adsorbed from yeast extract by fuller's earth plus (2) the antinemitic vitamin of Jansen and Donath or (3) other material which has many precipitation reactions in common with the Jansen and Donath vitamin but is not identical with it. In other words, at least three distinct and separable nutrilites may be involved in the growth stimulation of certain yeasts.

We shall now present evidence to show the existence of a fourth separable nutrilite which is concerned in the stimulation of the growth of yeast 578.

A highly concentrated preparation which was obtained from rice polish extract by adsorption on fuller's earth, precipitation with phosphotungstic acid, precipitation with silver nitrate and baryta, precipitation with chloroplatinic acid in absolute alcohol, using the method of Jansen and Donath, we shall for convenience designate as "A." It had a potency determined in accordance with a previous publication[12] of 125–200. A preparation of material from rice polish extract which was adsorbed by and extracted from fullers' earth, we shall designate as F. E. S. (fullers' earth solids). It has a potency of 2.5–3.

As a supplement to material which is not adsorbed from yeast extract by fuller's earth (U. R. Y.), "A" is (in accordance with their potencies) about 60 times as potent as "F. E. S." However, as a supplement to unadsorbed material from rice polish extract (designated as U. R. R.), "A" was shown to be only 20 times as potent as "F. E. S." This decideddiscrepancy which was obtained more than once led us to suspect that a new factor was present in the unadsorbed residue from yeast extract and in the "F. E. S.," but not to an appreciable extent in the unadsorbed residue from the rice polish extract.

The suspicions were confirmed when we prepared from the fuller's earth solid a preparation "F. E. S.$_5$" which supplements "A" plus "U. R. R." F. E. S.$_5$ was obtained by precipitating some of the fuller's earth solids with phosphotungstic acid in the presence of sulfuric acid and by subsequent removal of the excess acids and evaporation of the *filtrate*. Simultaneously

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[11] R. J. Williams, J. L. Wilson and F. H. Von der Ahe, THIS JOURNAL, **49**, 227 (1927).

[12] R. J. Williams and R. R. Roehm, *J. Biol. Chem.*, **87**, 581 (1930).

we decomposed the precipitated material with baryta and freed it from excess baryta. The precipitated material in this experiment is designated as "F. E. S.$_6$"

The behavior of the "F. E. S.$_5$" preparation in supplementing either "A" plus "U. R. R." or "F. E. S.$_6$" plus "U. R. R." is shown in Tables IV and V. The results obtained in these experiments were in each case confirmed by separate experiments which are not reported in detail.

TABLE IV

SUPPLEMENTARY ACTION OF "F. E. S.$_5$" ON "U. R. R." PLUS "A" (YEAST 578)

Addition to synthetic medium	Yeast crop Galv. deflection	Yeast crop Mg. of dry yeast
1 cc. of H_2O	37.65	0.26
8 mg. of "U. R. R." (in 1 cc. of H_2O)	31.65	.68
8 mg. of "U. R. R." + 0.005 mg. "A"	27.55	1.0
8 mg. of "U.R.R." + 0.2 mg. "F. E. S.$_5$"	29.8	0.87
8 mg. of "U. R. R." + 0.005 mg. "A" + 0.2 mg. "F. E. S.$_5$"	16.75	2.70

Seeding about 950,000 cells.

TABLE V

SUPPLEMENTARY ACTION OF "F. E. S.$_5$" ON "U. R. R." PLUS "F. E. S.$_6$" (YEAST 578)

Addition to synthetic medium	Yeast crop Galv. deflection	Yeast crop Mg. of dry yeast
1 cc. of H_2O	35.3	0.36
8 mg. of "U. R. R." (in 1 cc. of H_2O)	26.3	1.26
8 mg. of "U.R.R." + 0.1 mg. "F. E. S.$_5$"	25.1	1.38
8 mg. of "U.R.R." + 0.1 mg. "F. E. S.$_6$"	10.8	4.07
8 mg. of "U.R.R." + 0.1 mg. "F. E. S.$_5$" + 0.1 mg. "F. E. S.$_6$"	7.5	5.37
8 mg. of "U.R.R." + 0.2 mg. "F. E. S.$_5$"	25.25	1.37
8 mg. of "U.K.R." + 0.2 mg. "F. E. S.$_6$"	9.55	4.52
8 mg. of "U. R. R." + 0.2 mg. "F. E. S.$_5$" + 0.2 mg. "F. E. S.$_6$"	4.4	8.05

Seeding about 1,360,000 cells.

It will be noted in both cases that the addition of "F. E. S.$_5$" alone to "U. R. R." has very little effect but that its addition to (U. R. R. + F. E. S.$_6$) or (U. R. R. + A) has a very appreciable effect. Presumably the preparation "F. E. S.$_5$" contains the new factor relatively free from other known factors, but "F. E. S.$_6$" and other preparations probably contain some of the new factor and thus prevent the results from being as clear cut *as* they would otherwise be.

What the character of this new factor is or what relationship it may have to some of the components of vitamin B is largely conjecture. In view of the fact that the antineuritic vitamin may function as a yeast growth stimulant, it is entirely probable that other yeast growth stimulants of a similar nature may have some function in animal nutrition. It is certain that the study of yeast nutrilites and attempts to isolate them are not interesting alone from the standpoint of the yeast itself but also from the standpoint of higher organisms, since substances which stimulate yeast growth are present in practically all plant and animal tissues and may be presumed to have some function in these tissues.

We wish to acknowledge gratefully the support received for this research from the Research Council of the University of Oregon and from Standard Brands, Inc., Successors to the Fleischmann Company, etc.

Summary

1. Experiments with Wildiers' original yeast culture shows that his "bios" is not readily absorbed by fuller's earth and appears to be the same as the nutrilite which stimulates the growth of Gebrüde Mayer yeast. No conclusive evidence of its multiple nature is available.

2. The yeast nutrilites studied by W. L. Miller and his associates are shown to be distinct from the "bios" of Wildiers. The Toronto workers should be credited with the discovery of a new series of yeast nutrilites.

3. Yeast No. 578 of the American Type Culture Collection and old process baker's yeast appear to have more complex requirements than Wildiers' yeast. Evidence is presented for the existence of a fourth distinct nutrilite concerned in the growth stimulation of yeast No. 578. It seems reasonable to suspect that several of the nutrilites for this yeast may be components of "vitamin B," since the antineuritic vitamin has previously been shown to affect its growth very strikingly.

EUGENE, OREGON

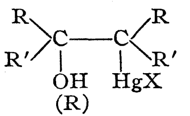
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE STRUCTURE OF THE COMPOUNDS PRODUCED BY THE ADDITION OF MERCURIC SALTS TO OLEFINS. II

BY ESTHER GRIFFITH AND C. S. MARVEL

RECEIVED DECEMBER 15, 1930 PUBLISHED FEBRUARY 9, 1931

Some time ago a communication[1] from this Laboratory described optically active isomers of an addition product of an olefin of the type RR'C=CRR' with a mercuric salt. The conclusion was drawn that the existence of these isomers furnished evidence for believing that such addition products should be represented by ordinary structural formulas (I) rather than as molecular addition products (II).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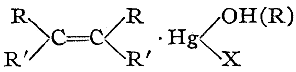
II

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[1] Sandborn with Marvel, THIS JOURNAL, 48, 1409 (1926).

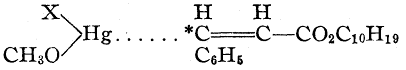
The particular products which have been described previously are two optically active isomers of *l*-menthyl β-methoxy-α-bromomercuri-hydrocinnamate (III) and two optically active isomers of I-menthyl β-methoxy-a-iodomercuri-hydrocinnamate (IV).

$C_6H_5CH(OCH_3)CH(HgBr)CO_2C_{10}H_{19}$ III $\qquad$ $C_6H_5CH(OCH_3)CH(HgI)CO_2C_{10}H_{19}$ IV

These products were prepared by adding mercuric acetate to I-menthyl cinnamate in methyl alcohol solution and converting the acetoxymercuri derivative thus obtained to the corresponding halide Since there are two asymmetric carbons produced by the addition of the methoxy and acetoxymercuri groups to the cinnamic ester, it is theoretically possible for four optically active forms of each of these addition products to exist. However, as is often the case in such addition reactions, all of these theoretically possible isomers were not obtained.

Although the isolation of two active isomers of each compound seemed sufficient to establish the fact that these substances were compounds whose structures could be represented best by ordinary valence bonds, it has seemed worth while to attempt to prepare other addition products which might yield the theoretical number of isomers. In the work described in this communication the unsaturated compounds studied were the I-menthylamide of cinnamic acid, d- and *l-sec.*-octyl cinnamates and d-bornyl cinnamate Only the last of these gave stable crystalline derivatives useful for the separation of isomers. However, here, as in the case of the *l*-menthyl cinnamate, only two optically active isomers were obtained.

Reference should be made to a suggestion by Piccard[2] in which he has pointed out that another assumption can be made which will account for two optically active isomers of such addition products without assuming that the mercury derivatives are of the ordinary valence type. This unusual assumption is that the addition product is represented by formula V.



$$\begin{array}{l} X \diagdown \\ \qquad \rangle Hg\ldots\ldots{}^*\overset{H}{C}=\overset{H}{C}-CO_2C_{10}H_{19} \\ CH_3O \diagup \qquad\quad \underset{}{C_6H_5} \end{array}$$

V

The carbon marked with the asterisk is a coordination center of a molecular addition product and may be optically active.

The work in this paper does not support or detract from this last suggestion but is further evidence of the fact that the addition products of mercuric salts and olefins are capable of optical isomerism.

Experimental Part

I-Menthylamide of **Cinnamic** Acid.—A solution of 16 g. of cinnamoyl chloride in 50 cc. of dry benzene was added slowly and with shaking to a solution of **31** g. of *l*-menthyl-

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[2] Piccard, private communication. See also Pfeiffer, *Naturwissenschaften,* 14, 1100 (1926).

amine in 100 cc. of dry benzene. The rate of addition was regulated so as to avoid marked increase in temperature. 2-Menthylamine hydrochloride separated from the solution. When the reaction was complete the mixture was filtered with suction and the precipitate of amine hydrochloride was washed with a little dry benzene. The benzene was evaporated from the filtrate and the amide was recrystallized from methyl alcohol. The yield was 13 g. (47% of the theoretical amount) of a product which melted at 158–159°.

Anal. Subs., 1.0010, 1.0010: 47.35, 47.2 cc. of $N/14$ HCl. Calcd. for $C_{10}H_{27}ON$: N, 4.9. Found: N, 4.73, 4.7.

Specific rotation. Solvent, methyl alcohol; subs., 0.5380, 0.5579; volume of solution, 15 cc.; length of tube, 1 dm.; temperature, 25°; **a**, −2.96°, −3.09°; $[\alpha]_D^{25}$ −82.3°, −82.9".

When the amide in methyl alcohol solution was treated with mercuric acetate, a compound containing mercury was obtained, but its instability rendered it unsuitable for fractional crystallization.

d- and *l*-2-Octyl Cinnamates.—A mixture of 11 g. of d-octanol-2 and 14 g. of cinnamoyl chloride was heated for two hours over a low flame. The resulting brown liquid was distilled under reduced pressure. There was thus obtained 16 g. (73% of the theoretical amount) of a product which boiled at 174–177° (5 mm). In the same way 13 g. of 1-octanol-2 and 18 g. of cinnamoyl chloride gave 12 g. (50% of the theoretical amount) of the levo isomer, b. p. 175–180° (6 mm.).

Analysis of the dextro isomer. Subs., 0.1611: CO_2, 0.4626; H_2O, 0.1337. Calcd. for $C_{17}H_{24}O_2$: C, 78.40; H, 9.29. Found: C, 78.31; H, 9.28.

The specific rotations were determined in ethyl acetate solution. d-Ester. Subs., 0.5645; volume of solution, 15 cc.; length of tube, 1 dm.; temperature, 30°; **a**, +1.6°; $[\alpha]_D^{30}$ +42.4°. I-Ester. Subs, 0.5164; volume of solution, 15 cc ; length of tube, 1 dm ; temperature, 27°; **a**, −1.49"; $[\alpha]_D^{27}$ −43.3°.

When either of the esters was treated with a methyl alcohol solution of mercuric acetate, reaction occurred, as shown by the absence of mercuric ions at the end of nine days. The addition products proved to be very low melting and were not isolated and purified as they were unsuited for extensive fractional crystallization. The addition products were treated with alcoholic sodium bromide but the bromo compounds were also too low melting to be satisfactory for fractional crystallization.

***d*-Bornyl Cinnamate.**—This ester was prepared in 85% yields from *d*-borneol and cinnamoyl chloride. The product thus obtained boiled at 200–202° at 6–7 mm. Minguin and Bollemont,[3] described the product as a solid melting at 33°. Hilditch[4] described it as a yellow liquid boiling at 226–230° at 27 mm. with a specific rotation of +29.05° in chloroform solution and +29.10° in acetone solution.

Specific Rotation. Solvent, methyl alcohol; subs., 1.4252, 1.3383; volume of solution, 15 cc., 20 cc.; length of tube, 1 dm., 2 dm.; temperature, 27°; **a**, +3.13°, +4.4°; $[\alpha]_D^{27}$ +32.8°, +32.9°. Solvent, ethyl acetate; subs., 2.2256; volume of solution, 20 cc.; length of tube, 2 dm.; temperature, 27°; α, +7.18; $[\alpha]_D^{27}$ +32.3°.

d-Bornyl β-Methoxy-α-acetoxymercuri-hydrocinnamate.—A solution of 10 g. of *d*-bornyl cinnamate in 20 cc. of absolute methyl alcohol was added to a solution of 11 g. of mercuric acetate in 100 cc. of absolute methyl alcohol. The reaction was complete after eight days at room temperature, The methyl alcohol was evaporated and the residue was washed with water and dried. The crude product was then analyzed and found to be the desired addition product.

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[3] Minguin and Bollemont, Compt. rend., 136, 238 (1903).

[4] Hilditch, J. Chem. *Soc.*, **93**, 7 (1908).

Anal. Subs., **0.1948:** Hg, **0.0667.** Calcd. for $C_{22}H_{30}O_5Hg$: Hg, **34.82.** Found: Hg, **34.24.**

The product thus obtained behaved like a mixture. After crystallization from methyl alcohol or petroleum ether the product melted over the range 90–100°. When the material was fractionated, samples were obtained which melted at 98–100°, **92–98°, 89–92°.** However, these fractions had almost the same specific rotations (+11.3°, +13.4° and 10.8°, respectively), and mixed melting point determinations showed that they were mixtures. Apparently the isomers of the acetate compound were not separated by crystallization.

***d*-Bornyl β-Methoxy-α-bromomercuri-hydrocinnamate.**—A solution of **20** g. of d-bornyl cinnamate in **50** cc. of absolute methyl alcohol was added to a solution of **22** g. of mercuric acetate in **250** cc. of absolute methyl alcohol. After two weeks the mixture was filtered to remove a small amount of precipitate and the methyl alcohol was evaporated under reduced pressure. The white solid was washed with water to remove acetic acid and mercuric acetate and dried. The yield of crude acetate was **45** g. This product was dissolved in about **200** cc. of absolute methyl alcohol and treated with a solution of **10** g. of sodium bromide in the same solvent. Crystals began to separate in a very short time. The first crop of crystals was filtered after one day. After recrystallization from petroleum ether this product melted at 131–132° (A). The next fraction to be isolated from the methyl alcohol was recrystallized from petroleum ether and it melted at 120–124°. Finally a third fraction (weighing **13** g.) of the addition compound was obtained. After recrystallization from petroleum ether it melted at 147–148° (B). A mixture of the first and third fractions melted at 120–125°. No further material separated from the reaction mixture even after standing for six months. About one centimeter of brown oil remained after the alcohol was evaporated.

The two bromo compounds were analyzed and rotations were determined.

Compound (A), m. p. **131–132°.**

Anal. Subs., **0.2484:** Hg, **0.0832.** Calcd. for $C_{20}H_{27}O_3HgBr$: Hg, **33.7.** Found: **33.5.**

Specific rotation. Subs., 0.1505; volume of solution, **15 cc.;** solvent, ethyl acetate; length of tube, 1 dm.; temperature, 25°; **a,** +0.17°; $[\alpha]^{25}_{D}$ +17.3°.

Compound (B), m. p. 147–148°.

Anal. Subs., **0.2332:** Hg, **0.0771.** Calcd. for $C_{20}H_{27}O_3HgBr$: Hg, **33.7.** Found: Hg, **33.1.**

Specific rotation. Subs., **0.1050;** volume of solution, **15** cc.; solvent, ethyl acetate; length of tube, **1** dm.; temperature, 25°; **a,** +0.10°; $[\alpha]^{25}_{D}$ +14.9°.

Summary

1. Two optical isomers of d-bornyl β-methoxy-α-bromomercuri-hydrocinnamate have been characterized.

2. The l-menthylamide of cinnamic acid and the d- and *l-sec.*-octyl esters of cinnamic acid have been characterized. The mercuric acetate addition products of these compounds were found to have physical properties which made it impractical to attempt to separate them into isomers by crystallization.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE POTENTIALS AND THE DECOMPOSITION REACTIONS OF ORTHO QUINONES IN ACID SOLUTION

BY LOUIS F. FIESER AND MARY A. PETERS[1]

RECEIVED DECEMBER 18, 1930 PUBLISHED FEBRUARY 9, 1931

With the development of a method of measuring accurately the potentials of unstable oxidation–reduction systems,[1a] it seemed desirable to apply this new method to a re-examination of some of the systems for which the reported values are in the nature of approximations. It is particularly difficult to characterize the systems from the ortho quinones by simple electrometric titration, because of the great instability of the oxidants. We have thus made use of the method of discontinuous titration in a further study of the ortho quinones derived from benzene, naphthalene and phenanthrene, and we have attempted wherever possible to establish the course of the reactions leading to the destruction of the oxidant.

β-Naphthoquinone

The instability of dilute solutions of this substance in alcoholic hydrochloric acid was noted by Conant and Fieser,[2] who reported the results of titrations of the oxidant and some preliminary observations concerning one of the decomposition products. In extending these results we first established the normal oxidation–reduction potential of the system by the discontinuous titration of pure β-naphthohydroquinone, with the results given in Table I. Solutions of the material were treated with varying quantities of an oxidizing agent and the initial potential in each experiment was established by extrapolation of the time–potential curve. The oxidizing agent employed was potassium molybdicyanide. With this reagent the potentials of the organic and inorganic systems are so close together

TABLE I

DISCONTINUOUS TITRATION OF β-NAPHTHOHYDROQUINONE (25°)

0.0003 **mol. eq. in** 220 **cc. of** 70% **alcohol,** 1 M **in** HCl **and** 0.2 *M* **in** LiCl, **required** 34.2 **cc. of** $K_3Mo(CN)_8$ **solution.**

Molybdicyanide soln., cc.	Initial potential, v.	Fraction of Mo soln. unreacted (m)	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Normal potential E_0, v.	Velocity constant, $\Delta E/t$
8	0.5623	0.008	0.302	0.5776	0.0003
10	.5653	.009	.408	.5768	.0003
12	.5673	.010	.532	.5754	.0003
14	.5705	.011	.680	.5755	,0004
16	.5732	.012	.859	.5751	.0003
18	.5764	.013	1.083	.5754	.0003
			Average	.5760	

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[1] This communication is in partial fulfilment of the requirements for the degree of Master of Arts at Radcliffe College.

[1a] Fieser, THIS JOURNAL, **52,** 4915 (1930).

[2] Conant and Fieser, *ibid.,* **46,** 1858 (1924).

that the oxidation of the hydroquinone does not go to completion and in calculating the correct ratio of oxidant to reductant (Column 4) the amount of unreacted reagent present (Column *3)* must be taken into consideration, as explained in the first paper cited. On account of this overlapping in potentials, no end-point can be obtained in acid solution. The β-naphthohydroquinone solution was thus compared with the molybdicyanide by titration in a neutral alcoholic buffer solution, for here the potential of the inorganic system is considerably higher than that of the other system. β-Naphthoquinone was found to be perfectly stable in this solution and we were thus able to use the continuous method of titration.

The velocity constants given in the last column of the table were calculated for a monomolecular reaction; they are numerically equal to the decrease in potential per minute. It may be noted that the decomposition of the oxidant was much slower than in the earlier work in which impure β-naphthoquinone was employed.

In order to study the products of the decomposition of β-naphthoquinone, we dissolved a quantity of the pure quinone in the alcoholic buffer solution and allowed the decomposition reaction to proceed to completion (about three hours). This solution was found to contain the oxidant of a stable system and the reductant of another, unstable system. The oxidant could be titrated with titanous chloride, hut the titration of the reductant presented a more difficult problem. Some indication of the normal potential of the unstable system was furnished by rapid titrations of the reductant with tetrabromo-o-benzoquinone The value found (0.576 v.) was very close to that of the β-naphthoquinone system (0.5760 v.), and the velocity of decomposition was identical with that noted. It was not possible, however, to carry out a discontinuous titration with molybdicyanide in just the manner described above, for on attempting to determine the end-point in neutral solution it was found that this oxidizing agent attacks the oxidant of the other stable system present. The same disturbing reaction prevented the use of ceric sulfate, which has a high enough potential to give an end-point in acid solution. Tetrabromo-*o*-benzoquinone is free from this objection, and has a sufficiently high potential, but the compound is not stable enough in solution to permit its use in the time-consuming discontinuous titration.

In order to make an evaluation of the normal potential which would be more reliable than that furnished by rapid titration, the following expedient was adopted. Portions of the solution of the decomposition products were treated with varying amounts of molybdicyanide solution and the initial potentials, velocity constants and the fraction of unreacted molybdicyanide (m) were obtained in the usual manner (Table II). The approximate value for the normal potential of 0.576 v. was then used to calculate from these results values for the ratio [Oxid]/[Red], and from these figures

TABLE II

TITRATION OF THE REDUCTANT FORMED IN THE DECOMPOSITION OF β-NAPHTHOQUINONE[a]

Molybdicyanide soln., cc.	Initial potential, v.	m	$\frac{[\text{Oxid}]}{[\text{Red}]}$	End-point, cc.	Normal potential, E_0, v.	Velocity constant, $\Delta E/t$
4	0.5612	0.007	0.311	16.7	0.5762	0.0003
6	.5694	.011	.589	15.9	.5769	0003
8	.5745	.013	.876	16.9	.5759	.0003
10	.5806	.016	1.41	16.8	.5761	.0004
12	.5863	019	2 19	17.1	.5751	.0004
			Average	16.7	Av. .5760	

[a] Solvent: See Table I.

values were obtained for the theoretical end-point of oxidation. The average end-point was then used to calculate values for the normal potential (next to last column). The constancy of the results, and the agreement with the approximate value, justifies this interpretation.

The normal potential found is the same as that for β-naphthoquinone (0.5760 v.), but it is also not far from the potential reported[2] for a known product of the acid decomposition of this quinone, namely, dinaphthyldiquinhydrone. A special study of this compound (see below) showed that the potential is indeed close to that found here, but that the compound is perfectly stable under the conditions of the experiment and that it is thus excluded as a possible product. On the other hand, a comparison of the values given in Tables I and II for both the normal potentials and the velocity constants leaves little doubt but that the reductant produced in the decomposition of β-naphthoquinone is β-naphthohydroquinone.

There remained the identification of the oxidant which is produced, and the determination of the relative amounts of the two decomposition products. The plan of attack was to reduce the oxidant and then to titrate in succession the reductant of each system with the same oxidizing agent. The reagent chosen was tetrabromo-o-benzoquinone. In each of the experiments listed in Table III a 20-cc. portion of the solution of the decomposition products was first titrated to an end-point with titanous chloride. This gave the value for the normal potential of the stable

TABLE III

TITRATION OF THE TWO DECOMPOSITION PRODUCTS OF β-NAPHTHOQUINONE[a]

Stable system			Unstable system			Molecular ratio of the two decomposition products: Col. 6/Col. 3
Titration of oxidant with $TiCl_3$, E_0, v.	Titration of reductant with $C_6Br_4O_2$ E_0, v.	End-point, cc	$C_6Br_4O_2$ soln. added, cc	Initial potential, v.	End-point calculated, cc.	
0.3560	0.3568	24.5	4	0.5547	25.0	1.02
.3570	.3568	25 4	8	.5660	25.5	1.00
.3558	.3572	23.4	10	.5722	23.5	1.00
.3572	.3572	29.6	10	.5674	29.8	1.01
.3562	.3569	24.2	12	.5755	24.6	1.02
.3568	.3568	23.1	16	.5859	23.3	1.01
.3562	.3572	23.7	20	.5952	24.5	1.03
Av. .3565	Av. .3569					Av. 1.01

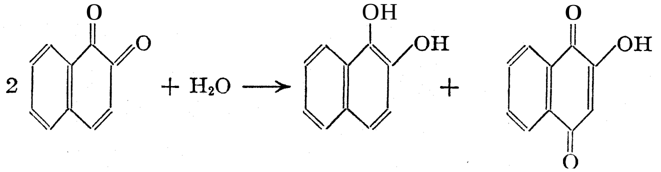
[a] Solvent: See Table I.

system listed in Column 1 of the table. A somewhat more reliable evaluation of the same potential was obtained when the reductant was then titrated with tetrabromo-o-benzoquinone, Column 2. At the conclusion of this titration a certain quantity of the oxidizing agent was quickly added and the potential was followed and extrapolated to zero time, giving the initial potential of the unstable system (Column 5). From this potential and the normal potential of the system the amount of oxidizing agent required for complete oxidation was calculated (Column 6). It is obvious that the amount of reagent consumed in the titration of the reductant of the stable system (Column 3) gives a measure of the quantity of the oxidant of that system which was originally present. It will be observed that the end-point of the titration is not the same in each experiment. This is because solutions of tetrabromo-o-benzoquinone in the alcoholic buffer are not altogether stable. A fresh solution was made up for each experiment, and in warming the solvent to effect dissolution, a certain variable quantity of the reagent was always destroyed. While separate experiments are thus not comparable, the titer of the quinone solution does not change appreciably in the short amount of time required to carry out the two separate titrations in each solution and the two end-points are strictly comparable. A comparison of the figures in Columns 3 and 6 thus gives a measure of the relative amounts of the two decomposition products formed, and this is indicated in the last column of the table. It is clear that the substances are produced in equimolecular proportion.

The potential of the more stable of the two systems (av., 0.3567 v.) suggests that the oxidant in question is 2-hydroxy-1,4-naphthoquinone. The value of 0.356 v. has been reported[2] for this compound, and we have found the average value of 0.3570 v. from a further series of determinations.[3] Any doubt as to the identity of the substance was dispelled by the isolation of hydroxynaphthoquinone from the solution.

The Mechanism of the Decomposition

The above results show that β-naphthoquinone in dilute alcoholic solution decomposes into equimolecular amounts of β-naphthohydroquinone and 2-hydroxy-1,4-naphthoquinone. While the final result thus represents a dispropdrtionation, there is further evidence which shows that the reaction does not follow the simple course:



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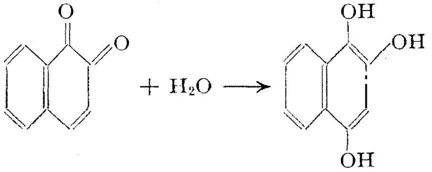
[3] The quinone was hydrogenated and titrated with potassium molybdicyanide. Individual results agreed within 0.1 mv.

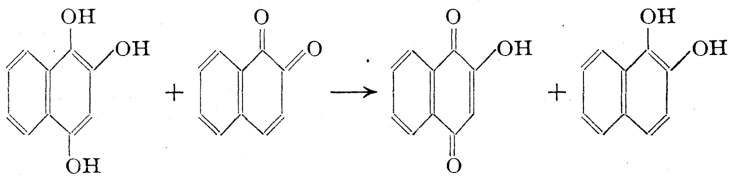
Such a reaction, in an aqueous–alcoholic medium, would be bimolecular. The reaction velocity measurements summarized in Tables I and II show, on the other hand, that the reaction is strictly monomolecular. The values obtained for the monomolecular constant agreed well in each individual experiment, as well as when the concentration of β-naphthoquinone was varied. A mechanism which postulates the intermediate formation of dinaphthyldiquinhydrone is likewise excluded, for this would be a bimolecular reaction.

The only mechanism which fits all of the facts is that β-naphthoquinone first adds a molecule of water as in I, and that the trihydroxynaphthalene

I (Slow)



II (Fast)



thus formed is oxidized at once by unchanged β-naphthoquinone, as in II. Oxidation–reduction reactions of the type of II are extremely rapid, and the speed of the first reaction thus controls the velocity of decomposition. Hydration of the ketonic substance is thus responsible for the final disproportionation in the present case. It may be noted that our results do not preclude the possibility that it is alcohol rather than water which adds to the quinone. If this reaction took place, it would lead to the formation of 4-ethoxy-1,2-naphthoquinone, a substance which would be hydrolyzed and isomerized to give 2-hydroxy-1,4-naphthoquinone under the conditions of the experiment.[4]

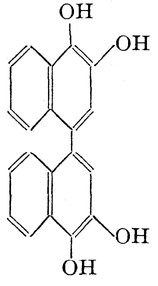
It is a well-known fact that β-naphthoquinone can be converted almost quantitatively into dinaphthyldiquinhydrone by the action of mineral acids, and yet no trace of this material was detected in the present experiments. The difference is easily accounted for. When a small amount of β-naphthoquinone is dissolved in a large amount of alcoholic acid, as in our experiments, the monomolecular reaction consumes the material. The reaction is slow and it is not accelerated by increasing the concentration of the reactant. Thus when a large amount of the quinone is stirred into a relatively small quantity of acid, the speed of the monomolecular reaction remains unchanged, while the condensation of two molecules of the quinone

[4] Fieser, This Journal, 48, 2922 (1926).

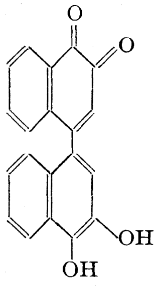
to give dinaphthyldiquinhydrone, being a bimolecular reaction, is greatly accelerated.

Dinaphthyldiquinhydrone (IV) and Dinaphthyldiquinone (V)

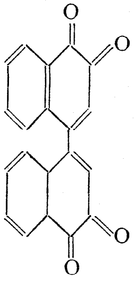
Since the compounds named are ortho quinones, they are appropriately included in this study. When dinaphthyldiquinhydrone, III, was titrated in alcoholic acid solution with ceric sulfate, a curve was obtained having two distinct inflections, as shown in Fig. 1 The reactants present appeared to be perfectly stable and no drift in the potentials was observed except at the very end of the titration. This drift is attributable to an oxidation of the solvent alcohol by ceric sulfate when an excess of the latter is present. The lower half of the curve refers to the potentials of the system formed by the reductant, III, and the monoquinone, IV, for a similar curve was obtained by the titration of the latter substance with titanous chloride. The upper half of the double curve obviously refers to the equilibrium between the monoauinone and the diquinone, V. The complete curve has a distinct end-point, and the "end-point" of each single curve can be taken as half of this value; but it is not permissible to take as the normal potentials of the two systems the mid-points of the two curves, for the normal potentials lie so close together that at almost



III



IV



V

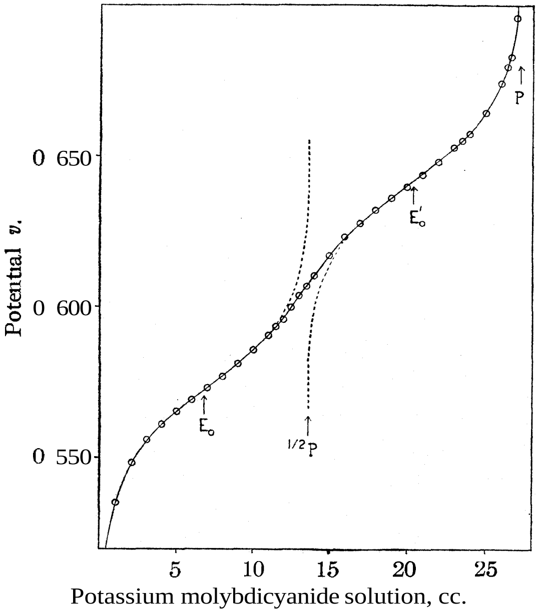


Fig. 1.—The titration of dinaphthyldihydroquinone.

any potential level all three of the organic substances are present in finite concentration. Such approximate values for the normal potentials were, however, employed in calculating more reliable figures in the following manner. From each of the potentials of the lower system, and the approximate normal potential of the upper system, we calculated the amount of diquinone present, and thus the true ratio of the monoquinone to its reductant. This permitted a calculation of the normal potential of the lower system from each observation. The process was then reversed, and the normal potential of the upper system was calculated. A summary of a few calculations from the results which are reported graphically in Fig. 1 is given in Table IV. In Fig. 1 the dotted lines represent the theoretical potentials of the two systems if each were free to function independently; it is obvious that the experimental curve is the resultant of these two.

Table IV

Titration or Dinaphthyldihydroquinone (25°)

Solvent: 70% alcohol, 1 M **in** HCl, 0.2 **M in** LiCl. **End-point of complete oxidation** = 27 2 **cc. of ceric sulfate solution.**

Monoquinone system Ceric sulfate soln., cc.	Potential, v.	Fraction, m	Normal potential, v.	Diquinone system Ceric sulfate soln., cc.	Potential, v.	Fraction, m	Normal potential, v.
2	0.5483	0.001	0.5709	16	0.6231	0.018	0.6431
4	.5610	.002	.5723	18	.6321	.009	.6416
6	.5693	.003	.5724	20	6397	.006	.6413
8	.5771	.005	.5727	22	.6480	.003	.6420
10	.5857	.012	.5731	24	.6573	,002	.6423
		Av.	.5723			**Av.**	.6420

3,4-Phenanthrenequinone

The normal potential of the unstable system formed by morphol and its oxidation product was determined in exactly the same manner as in the case of β-naphthohydroquinone. The explanation given of Table I thus applies equally well to the results listed in Table V. The normal potential

Table V

Discontinuous Titration of Morphol (25°)

0.0003 **Mol. eq. in** 220 **cc. of** 70% **alcohol,** 0.5 M **in** HCl **and** 0.2 **M in** LiCl, **required** 25.2 ***cc.* of** $K_3Mo(CN)_8$ **solution**

Molybdicyanide soln., cc.	Initial potential, v.	Fraction of Mo soln. unreacted (*m*)	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Normal potential, v.	Velocity const., $\Delta E/t$
2	0.5906	0.035	0.083	0.6227	0.0003
4	.6007	.051	.177	.6228	.0003
6	.6055	.060	.289	.6214	.0003
8	.6093	.069	.419	.6205	.0003
10	.6140	.082	.573	.6211	.0003
12	.6175	.094	.759	.6208	.0003
14	.6212	.105	.989	.6213	.0003
			Av.	.6215	

of this system is so close to that of the molybdicyanide system (0.6760 v.) that at the mid-point of the titration as much as 10% of the molybdicyanide fails to react and remains in the equilibrium mixture. The correction which must be applied to give the true ratio of organic oxidant to reductant is thus large and there is more uncertainty about the value found for the normal potential than in the previous cases studied. In order to obtain the most reliable results possible, we thus confined our experiments to measurements at the lower potentials.

The decomposition products of 3,4-phenanthrenequinone were studied by the method described in connection with Table III, above, and the results are included in Table VI. In the present case it was found that when the oxidant of the stable system was titrated with titanous chloride, the electrode equilibrium was not good and the values thus found for the normal potential are less reliable than those obtained in the back titration and they are not reported. A further variation from the other procedure was that we employed a single series of measurements for the calculation of the normal potentials, as well as of the relative concentrations, of the two decomposition products This was possible because all the indications were that the reductant which is produced in the decomposition is morphol. We thus used the normal potential found for the system from this compound in calculating from each initial potential for the unstable system the amount of oxidizing agent which would be required for complete oxidation. These figures are given in Column 6, and *a* comparison with the end-points in the titrations of the stable reductant (Col. 2) gives the relative proportion of the two decomposition products (Col. 7). Having established the ratio between the concentrations of these products, the titer of the stable reductant could be regarded as a standardization of the tetrabromo-o-benzoquinone solution in each experiment. The ratio of the

TABLE VI

TITRATION OF THE TWO DECOMPOSITION PRODUCTS OF 3,4-PHENANTHRENEQUINONE[a]

Stable system — Titration of reductant with $C_6Br_4O_2$		Unstable system					**Unstable system**	
E_0, v.	End-point, cc.	$C_6Br_4O_2$ **soln.** added, **cc.**	Initial potential, v.	Velocity constant	End-**point** calcd., cc.	**Mol.** ratio of **decomp.** products **Col. 6/Col.** 2	$\frac{[\text{Oxid}]}{[\text{Red}]}$	E_0, v.
0.3976	24.7	6	0.6049	0.0003	27.8	1.12	0.280	0.6212
.3972	24.8	10	.6137	.0003	28.0	1.13	.571	.6209
.3972	26.3	12	.6162	.0003	30.1	1.14	.698	.6208
.3974	24.3	14	.6220	.0003	27.4	1.13	1.08	.6211
.3978	25.2	16	.6246	.0003	28.4	1.13	1.33	.6209
Av. .3974						Av. 1.11		Av. .6210
After an interval of 30 hours								
0.3980	24.6	10	0.6121	0.0003	30.9	1.26		

[a] Solvent, see Table V.

components of the unstable system was then calculated from the expression: [Oxid]/[Red] = (oxid. agent added)/[(titer of stable Red) × 1.11 − (Oxid agent added)]. The normal potential was then calculated from these values (see last column).

The normal potential of 0.3974 v. found for the more stable of the two systems is sufficiently close to the value of 0.396 v. reported for 3-hydroxy-1,4-phenanthrenequinone[5] to show that one of the decomposition products of the ortho quinone under consideration is the corresponding hydroxy-*p*-quinone. The potential of the unstable system agrees well with that found for the system morphol/3,4-phenanthrenequinone. The identity of the two decomposition products thus seems clear. There is one point of difference, however, from the results obtained with β-naphthoquinone. The amount of the hydroquinone is in excess of the amount of the hydroxyquinone. The experiment reported in the last line serves to account for this difference. It shows that when the solution was allowed to stand for over a day, the relative proportion of the hydroxyquinone was even less than in the experiments carried out in succession on a solution prepared twelve hours in advance. It is known that 3-hydroxy-1,P-phenanthrenequinone undergoes cleavage very readily in alkaline solution,[6] and that it differs in this respect from hydroxynaphthoquinone. It now appears that acid cleavage is also possible. A certain quantity of the material was destroyed by cleavage during the time allowed for the completion of the decomposition reaction; a further amount had been destroyed during the thirty-hour period.

This interpretation of the experiments leads to the conclusion that the mechanism of the decomposition of this ortho quinone is exactly like that of β-naphthoquinone.

It is worth noting that the value found for the normal potential of the 3,4-phenanthrenequinone system by a method which involves a rather large correction factor (Table V) is well confirmed by the results of Table VI, in which no such correction was required. The value of 0.621 v. thus may be accepted as a reliable constant to replace the approximate figure of 0.615 v. reported by one of us.[5]

1,2-Phenanthrenequinone

Since there is apparently a considerable error in at least one of the earlier, admittedly approximate, determinations, it seemed advisable to reinvestigate other ortho quinone systems by the discontinuous titration method. The results for one of these are given in Table VII. The potential here is so high that potassium molybdicyanide cannot be used as a titrating agent, and tetrabromo-o-benzoquinone is not stable enough to use

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[5] Fieser, THIS JOURNAL, 51, 3101 (1929).

[6] Fieser, *ibid.*, 51, 940 (1929).

TABLE VII

DISCONTINUOUS TITRATION OF 1,2-DIHYDROXY-PHENANTHRENE (25°)

0.0003 Mol. eq. in 220 cc. of 70% alcohol, 0.5 M in HCl and 0.2 *M* in LiCl, required 23.6 cc. of ceric sulfate solution.

Ceric sulfate soln., cc.	Initial potential, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Velocity constant	Normal potential, v.
4	0.6380	0.204	0.0003	0.6584
6	.6446	.291	.0004	.6604
8	.6514	.513	.0004	.6600
10	.6563	.735	.0005	.6602
12	.6605	1.03	.0005	.6599
14	.6651	1.46	.0006	.6603
18	.6762	3.22	.0006	.6612
				Av. .6601

in the discontinuous titration method. We consequently used ceric sulfate even though the reaction of this substance with alcohol near the end-point of the titration introduces a slight uncertainty regarding the end-point. The new value, however, is certainly more reliable than that previously reported.[5]

Ortho Benzoquinone

Since ortho benzoquinone and catechol are soluble in water, this solvent was used in carrying out titrations of catechol so that ceric sulfate could be used as the oxidizing agent without any disturbing reaction of this reagent with the solvent. The results given in Table VII do not differ materially from those which have been obtained with other systems. There is a slight trend in the uncorrected values for the normal potential and it is in such a direction as to indicate an association between the oxidant and the. reductant. A correction factor, c, was consequently applied in the manner explained before.' The velocity constants correspond well with the requirements for a monomolecular decomposition reaction. We did not investigate the reaction further, because we were unable to find a satisfactory method of establishing the normal potential of the probable decomposition product.

Conant and Fieser[2] carried out rapid titrations of ortho benzoquinone with titanous chloride and obtained the values of 0.786 v. and 0.776 v. for 0.1 N and 1 N hydrochloric acid solutions, respectively. The present results show that these early figures are much too low. There does appear to be some slight increase in the potential with decreasing acidity of the solution. The potential of the system in neutral buffer is probably somewhat greater than 0.794 v. In a neutral alcoholic solution a potential about ten millivolts higher would be anticipated. Thus the value of 0.810 v. which was estimated by one of us[7] by a purely indirect method does not appear to be very far in error.

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[7] Fieser, THIS JOURNAL, 52, 5204 (1930).

TABLE VIII

DISCONTINUOUS TITRATIONS OF CATECHOL WITH CERIC SULFATE (25°)

A. Solvent: 0.5 N H_2SO_4; end-point, 25.0 cc.

Ceric sulfate soln., cc.	*Initial* potential, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Correction factor, c	Velocity const.	Normal potential, Eo uncorr.	Normal potential, Eo corr.
3	0.7676	0.136	1.03	0.0006	0.7932	07941
4	.7719	.191	1.04	0006	.7932	7937
5	.7760	,250	1.02	.0006	.7938	.7942
6	.7790	.316	1.02	.0006	.7938	.7942
7	.7822	.388	0.98	.0007	.7943	.7947
8	.7847	.471	.97	.0006	7943	.7946
9	.7867	.564	1.10	.0007	.7941	.7943
12	.7944	.923		.0008	.7943	7943
15	.8001	1 60	1.15	0008	.7919	.7947
		Av.	1.03		Av.	.7943

B. Solvent: 1 *N* H_2SO_4; end-point, 20.4 cc.

Ceric sulfate soln., cc.	*Initial* potential, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Correction factor, c	Velocity const.	Normal potential, Eo uncorr.	Normal potential, Eo corr.
4	0.7682	0.244	1.15	0.0005	0.7863	0.7894
6	.7770	.417	1.17	.0005	.7882	.7890
8	.7826	.645	1.14	.0006	.7882	.7891
10	.7888	.962	..	.0007	.7891	.7891
12	.7950	1.43	1.30	.0008	.7904	.7896
14	.7996	2.19	1.06	.0008	.7896	.7889
16	.8089	3.64	1.20	.0010	.7933	.7895
		Av.	1.17		Av.	.7891

Experimental Part

Materials.—From a review of the literature it seems clear that neither β-naphthoquinone nor its reduction product has been prepared in completely pure form. After many trial experiments we concluded that the most promising source of such samples was 1,2-diacetoxynaphthalene. In preparing this compound by the reductive acetylation of ordinary samples of β-naphthoquinone[8] a certain amount of dinaphthyldiquinhydrone was always formed and this itself underwent acetylative reduction. The amount of the by-product may be reduced to a minimum by adding the quinone in small portions to a mixture of sodium acetate, acetic anhydride and zinc dust and by adding fresh portions of zinc dust as required to insure the rapid decolorization of the quinone. The crude product obtained was always oily. It was treated with ether, which left a residue of the solid tetra-acetate of dinaphthyldihydroquinone. The ethereal solution was washed well with sodium carbonate and dried over calcium chloride. Evaporation of the ether left a greenish-black oil which is not easily purified by crystallization. The material distils well, however, at diminished pressure, and after two distillations a colorless product was obtained. The 1,2-diacetoxynaphthalene formed small, colorless crystals from alcohol; yield 50%; m. p. 109.5° (Korn, 102-104°).

For the hydrolysis of the diacetate in the absence of oxygen, and for many similar operations, we have found the following simple apparatus to be of great service. The reaction vessel was a three-necked flask, carrying through one opening a tube for the admission of purified nitrogen. Through the central opening a tube was inserted which ordinarily served as the outlet for nitrogen but which could be pushed to the bottom of the flask when it was desired to transfer a solution to another piece of apparatus under

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[8] Compare Korn, Ber., 17, 3025 (1884).

pressure of nitrogen gas. The third tubulature carried a separatory funnel for the admission of solution. In order to sweep this solution free of oxygen, a tube extending to the bottom of the funnel was connected to the nitrogen outlet by a length of rubber tubing. The glass tube passed through a large tube which was inserted in the stopper of the funnel, and through which, by means of a side-T, the nitrogen escaped. The advantage of the arrangement is that different reagents may be freed of oxygen rapidly and introduced in succession to the reaction flask.

For the preparation of pure *β-naphthohydroquinone* 10 g. of 1,2-diacetoxynaphthalene was dissolved in 75 cc. of alcohol, the solution was swept with nitrogen and treated with a solution of 8 g. of sodium hydroxide in 50 cc. of water. When the hydrolysis was complete the faintly yellow solution was acidified with 130 cc. of 1 M hydrochloric acid, and diluted with about 400 cc. of oxygen-free water. The material crystallized on cooling in the form of large colorless plates melting at 105.5° (4 g.). The melting point of 60° reported for samples of this compound prepared by reduction of the quinone[9] indicates that this is not a satisfactory method of preparation. By adding an excess of ferric chloride to the mother liquor from the above crystallization, the remaining material was converted into an excellent sample of crystalline β-naphthoquinone (2.6 g.).

Pure **β-naphthoquinone** may be obtained by oxidation of the pure hydroquinone under carefully controlled conditions. Five-tenths g. of β-naphthohydroquinone was dissolved in 10 cc. of alcohol and a mixture of 10 cc. of concentrated hydrochloric acid and 25 cc. of water was added. The solution was cooled to 0° and poured into a cooled solution of 100 cc. of 1 M ferric chloride solution also at 0°. The quinone soon began to separate in the form of small orange needles and crystallization was complete in about ten minutes, when the material was collected and washed well with water. In its crystalline character, orange color and freedom from all traces of foreign material, this product differs markedly from the samples obtained by the usual method of preparation. While our attempts to hydrogenate ordinary samples of the compound were no more successful than those of Skita and Rohrmann,[10] the pure quinone was found to be easily reduced by this method.

The preparation of pure morphol[11] and 3,4-phenanthrenequinone[6] have been described. An improved method of preparing *1,2-dihydroxy-phenanthrene*[12] was as follows. The corresponding quinone was reduced in glacial acetic acid solution with zinc dust and the colorless solution was filtered by suction into water. The gray product which separated was distilled in vacuum, thereby removing most of the color. Crystallization from benzene–ligroin gave colorless needles melting at 178". The sample did not darken on storage.

Details of the Measurements.—The solutions of the hydroquinone used in carrying put the titrations reported in Tables I. V and VII were prepared by placing the weighed solid in the three-necked flask referred to above, and adding the oxygen-free buffer solution after removal of all of the oxygen from the flask. The solution was then transferred to a protected reservoir buret of the type described by Cohen,[13] but modified by providing a tip below the lower stopcock through which the solution can enter the buret. This eliminates much delay in drainage. It is convenient to prepare 250 cc. of a solution of such concentration that 20 cc. contains 0.0003 mol. eq, of the reductant. In each experiment this amount was measured into 200 cc. of the buffer solution contained in the electrode vessel and swept free of oxygen.

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[9] Liebermann and Jacobson, *Ann.*, **211**, 58 (1882).

[10] Skita and Rohrmann, *Ber.*, 63, 1473 (1930).

[11] Fieser, Ref. 6. Further details will be published elsewhere.

[12] Fieser. THIS JOURNAL. 51, 1896 (1929).

[13] Cohen, *Ind. Eng. Chem.*, 20,1238 (1928).

Aqueous solutions of potassium molybdicyanide and solutions of ceric sulfate in either 1 N or 0.5 N sulfuric acid were employed. The tetrabromo-*o*-benzoquinone was dissolved in the buffer solution with which it was to be used.

Solutions of the decomposition products were prepared by adding the appropriate quinone to the oxygen-free buffer solution. The mixture was shaken well to prevent the formation of any saturated solution during the process of dissolution, and the solution was allowed to stand for five to twelve hours in an atmosphere of nitrogen. During this time the solution of β-naphthoquinone lost its original deep amber color and became pale yellow. The solution of 3,4-phenanthrenequinone remained somewhat red to the end. The solutions were made up to contain approximately 0.0003 M of the quinone in 20 cc., the amount used in each experiment.

Hydroxynaphthoquinone was isolated from the solution prepared from β-naphthoquinone by extracting the diluted solution with ether, washing the ether well with water and then extracting with sodium carbonate solution. The soda-soluble material was recovered by extraction of the acidified solution with ether. The product, which melted with decomposition at 194°, was identified by conversion into the ether, m. p. 183.5°, and comparison of an authentic sample, mixed m. p. 183.5°.

For details concerning the potential measurements and the interpretation and calculation of results reference may be made to the first paper cited for no changes in the general procedure were introduced. The values found for the normal potentials of the molybdicyanide system in 70% alcoholic solutions were as follows: 0.5 M acid, 0.6760 v.; 1 M acid, 0.6867 v.

Summary

By means of potentiometric analysis it has been found that β-naphthoquinone decomposes in dilute acid solution to give equal parts of β-naphthohydroquinone and hydroxynaphthoquinone. Since the reaction is monomolecular, it is concluded that the first step in the disproportionation is the addition of the elements of water to the quinone. 3,4-Phenanthrenequinone behaves in a similar manner, and it is presumed that the reaction is characteristic of all of the unsubstituted ortho quinones.

The method of discontinuous titration has been used in obtaining values for the normal oxidation–reduction potentials of the ortho quinones derived from benzene, naphthalene and phenanthrene, and the results are considered to supplant the earlier, less reliable, determinations.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

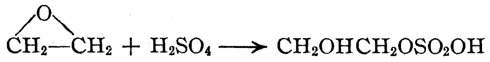
REACTIONS OF HETEROCYCLES WITH PHENOLS. STUDIES IN THE REACTION OF ETHYLENE OXIDE WITH PHENOL

BY RICHARD A. SMITH AND JOSEPH B. NIEDERL

RECEIVED DECEMBER 20, 1930 PUBLISHED FEBRUARY 9, 1931

A survey of the literature to date reveals the following reports of interactions of phenols with heterocyclic compounds: (1) ethylene oxide, the simplest oxygen heterocycle, under the influence of heat combines with phenol to yield (β-hydroxy-ethyl)-phenyl ether. The same phenoxy compound can be obtained from ethylene chlorohydrin and sodium phenoxide.[1] Epichlorohydrin and phenol under the influence of heat yield the analogous phenyl ether.[2] (2) In the field of nitrogen heterocycles, reactions have been reported with diazomethane,[3] isatin[4] and alloxan.[5] Ethylene-imine and its homologs, as being structurally related to the ethylene oxide studied in this paper, are under investigation.

In the following investigation ethylene oxide was caused to react with phenol in the cold and in the presence of sulfuric acid to form, not an ether, as would be indicated by the work cited, but a substituted phenol. This product appears to be o-vinylphenol, for which the following proofs of structure are offered. (1) The explanation here given for a reaction mechanism appears to be well justified; it may be assumed that the first step in the reaction is the addition of sulfuric acid to ethylene oxide to form ethanol sulfuric acid according to the equation



$$\overset{O}{CH_2—CH_2} + H_2SO_4 \longrightarrow CH_2OHCH_2OSO_2OH$$

The resulting compound then reacts with phenol to form (β-hydroxy-ethyl)-phenyl ether with the elimination of sulfuric acid

$$CH_2OHCH_2OSO_2OH + HOC_6H_5 \longrightarrow H_2SO_4 + CH_2OHCH_2OC_6H_5$$

Inasmuch as ethylene oxide and phenol under the action of heat and pressure form this compound, it is plausible to assume the formation of it here, as an intermediate, with the sulfuric acid acting in the capacity of a catalyst. Phenolic ethers with a negative group in the side chain, as in the foregoing case, rearrange readily in the presence of mineral acids to form substituted phenols. We assume this to be the case here with the formation of *o*-hydroxyphenylethyl alcohol

$$CH_2OHCH_2OC_6H_5 \longrightarrow CH_2OHCH_2C_6H_4OH$$

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[1] Roithner, Monatsh., 15, 674 (1894).

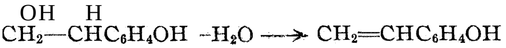
[2] Lindeman, *Ber.*, 24, 2146 (1891); E. Fischer and Kramer, *ibid.*, 41, 2730 (1908).

[3] Pechmann, *ibid.*, 28, 857 (1895).

[4] Baeyer and Lazarus, *ibid.*, 18, 2641 (1895); Liebermann and Danaila, *ibid.*, 40, 3593 (1907).

[5] Bohringer, German Patents 107,720 and 115,817.

The presence of concentrated sulfuric acid causes dehydration with the formation of o-vinylphenol



$$\overset{\text{OH}}{\text{CH}_2}\text{—}\overset{\text{H}}{\text{C}}\text{HC}_6\text{H}_4\text{OH} - \text{H}_2\text{O} \longrightarrow \text{CH}_2{=}\text{CHC}_6\text{H}_4\text{OH}$$

As a modification of the foregoing mechanism, dehydration of the phenoxy glycol may precede rearrangement. It has been shown that unsaturated ethers of the type which would thus be formed rearrange very readily to give ortho substituted phenols.[6] (2) The physical and chemical constants of the compound obtained corresponded with those given in the literature for o-vinylphenol. For further identification, two derivatives, the $3,5,1^1,1^2$-tetrabromo-2-hydroxyethylbenzene and the o-vinylphenoxyacetic acid, were prepared; the physical properties of these also agreed with those given in the literature.

In order, however, to substantiate more fully the reaction mechanism offered, the o-vinylphenol was synthesized by a different method as follows.

Ethylene chlorohydrin was treated with potassium phenoxide and the corresponding (β-hydroxy-ethyl)-phenyl ether obtained; this same ether can also be obtained by the action of ethylene oxide on phenol. The ether was then treated with concentrated sulfuric acid in a manner analogous to that used in the phenol–ethylene oxide condensation. The product was worked up as before and proved to be o-vinylphenol with the same physical constants and yielding the same derivatives. This indicated that the rearrangement and dehydration assumed in the proposed mechanism are allowable. The reaction is also of general interest as it substantiates the explanation offered in the condensation reactions taking place in the cold between unsaturated compounds (hydrocarbons, alcohols, esters, ethers, aldehydes, acetals, ketones, acids, nitriles, amines and halides) with phenols in the presence of concentrated sulfuric acid.[7]

Experimental

(1) Vinylphenol from Ethylene Oxide and Phenol.—A fifth mole of concentrated sulfuric acid was slowly added with cooling to a solution of molar quantities of phenol and ethylene oxide. The action during addition was vigorous. The containing flask was then closed with a stopper containing a calcium chloride drying tube and allowed to stand for one week. The product was washed with cold water to remove phenol, ethylene oxide, sulfuric and sulfonic acids and other water-soluble by-products. o-Vinylphenol is slightly soluble in water. The resulting liquid was distilled in vacuo. Redistillation yielded pure o-vinylphenol in about 65% yield. It was found that hydroquinone was a good inhibitor to polymerization. The rate of reaction as well as the yield of product can be controlled by the amount of sulfuric acid used. Pure o-vinylphenol melts at 29–29.5° (corr.) and boils at 56° under a pressure of 4 mm. The boiling point given by Fries and Fickewirth of 108° at 15 mm. is incorrect for the pure product,

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[6] Claisen and Eisleb, ***Ann***, 401, 21 (1914); Ber., 58, 275 (1925).

[7] Niederl and Natelson, THIS JOURNAL, 53, 272 (1931).

which at that pressure boils at 77°. Upon distilling o-vinylphenol from the polymerized product a temperature approximating that given by Fries and Fickewirth is noted.[8]

(2) **3,5,1^1,1^2-Tetrabromo-2-hydroxy-ethylbenzene.**—*o*-Vinylphenol, as prepared above in a chloroform solution, was treated with an excess of bromine with cooling. After the action had subsided, the hydrogen bromide, excess bromine, and chloroform were driven off with heat and the remaining solid purified by recrystallization from benzene. The final product melted at 105°, which is in agreement with the literature.

(3) o-Vinylphenoxyacetic Acid.—Molar quantities of o-vinylphenol, as prepared above, and bromoacetic acid were allowed to stand at room temperature in an alkaline solution for a few hours. The solution was then acidified and the resulting product purified by recrystallization from benzene or dilute alcohol. Prisms melting at 137° were obtained. This also was in agreement with the literature.

(4) **(β-Hydroxy-ethyl)-phenyl** Ether.—Molar quantities of potassium phenoxide and ethylene chlorohydrin were heated at 150° for six hours, and after cooling and filtering the liquid was distilled in vacuo. The fraction boiling at 163–167° at 80 mm. was retained as being the desired phenoxy glycol.

(5) o-Vinylphenol from **(β-Hydroxy-ethyl)-phenyl** Ether.—A molar quantity of the phenoxy glycol was allowed to stand for one week at room temperature with a fifth molar quantity of concentrated sulfuric acid. The product was washed with water and distilled in vacuo. o-Vinylphenol with the same boiling point as previously given was obtained; it formed the same bromine and acetic acid derivatives, proving that the compounds prepared by the two different methods were identical.

Summary

1. Ethylene oxide reacts with phenol in the cold in the presence of concentrated sulfuric acid to yield an ortho substituted phenol.

2. A probable mechanism for the above reaction has been advanced and reasons substantiating it have been given.

3. Two new methods for the preparation of o-vinylphenol have been discussed.

NEW YORK, N. Y.

NOTES

The Optical Activity of Cystine Preparations Used for Animal Experimentation.—Marston and Robertson[1] have recently expressed the opinion that much of the confusion in the literature dealing with cystine metabolism might have been avoided by determining the optical activity of the preparations used and have severely criticized certain studies on this account.

For several years we have been using cystine, prepared from human hair, in animal feeding experiments. Most of our preparations, as well as a number of student preparations subsequently reprecipitated by the author,

[8] Fries and Fickewirth, *Ber.*, 41, 370 (1908)

[1] Marston and Robertson, "The Utilization of Sulfur by Animals," Commonwealth of Australia, Council for Scientific and Industrial Research, Melbourne, 1928, Bulletin No. 39, 51 pp.

have been tested for their optical activity. All of these preparations were made for use in animal experimentation, and not for the determination of precise physical and chemical constants. It occurred to the writer that this information might furnish a rough index of the validity of Marston and Robertson's criticisms.

The method of isolation was essentially that outlined by Morrow.[2] The isoelectric precipitations were controlled with Congo red and litmus papers. The student preparations had been precipitated only once from the more or less successfully decolorized solutions, and varied considerably in color and tyrosine content. These preparations were subsequently reprecipitated by the author.

After drying, 1 g. of each of the above preparations was made up to 100 ml. in N hydrochloric acid, analyzed for sulfur and polarized at 21°. The accompanying table shows the results obtained.

Sample	S, %	$[\alpha]^{21}_{D}$	Remarks
158	26.02	$-212.3°$	Author's preparation
159	26.02	$-212.3°$	Student preparation
160	26.34	$-210.4°$	Student preparation
161	25.91	$-208.4°$	Student preparation
162	26.14	$-207.4°$	Student preparation
163	26.53	$-185.9°$	Student preparation
164	26.40	$-210.0°$	Student preparation
177	26.48	$-216.6°$	Author's preparation

It is obvious that the variations in specific rotation cannot be explained on the basis of sulfur content. It is highly probable that any of these samples, with the exception of No. 163, is suitable for animal feeding unless it is assumed that inactive cystine is highly toxic. Subsequent treatment of Sample No. 163 indicated that the above variations in specific rotation are partly due to the prolonged washing of certain samples with hot water in order to remove the tyrosine present.

CONTRIBUTION FROM THE
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CORVALLIS, OREGON

J. R. HAAG

RECEIVED NOVEMBER 10, 1930
PUBLISHED FEBRUARY 9, 1931

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p-Cymene Studies. XIV. **p-Cymylhydrazine-2.**—This note is an extension of a paper by Wheeler and Thomas [THIS JOURNAL, 51, 3135 (1929)]. Additional salts such as the acetate, oxalate, lactate and benzoate and a condensation product with m-nitrobenzaldehyde have been prepared. Unstable products were obtained with formaldehyde, acetalde-

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[2] Morrow, "Biochemical Laboratory Methods," John Wiley and Sons, Inc., New York, 1927, p. 140.

hyde, propional, heptaldehyde, chloral, furfural, o-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde, anisaldehyde, ethyl acetoacetate, mesityl oxide, cyclohexanone, carvone and benzoylacetone. The products were reddish, viscous oils which did not crystallize at −30°. No reaction seemed to take place with *p*-hydroxybenzaldehyde, piperonal, vanillin and camphor. *p*-Cymylhydrazine cannot therefore be regarded as a good reagent for the carbonyl group.

Experimental.—The frequent appearance of tar, causing varying yields of cymylhydrazine, led to the observation that the acid concentration in the reduction process is very important. The proper acid concentration was obtained by running the sulfur dioxide into the sodium hydroxide solution until it was neutral and then continuing the passage of the gas for a period equal to one-tenth of the time required for neutralization. The free base did not change color in well-stoppered bottles.

TABLE I

PREPARATIONAL DATA

	Salt	Crystal form	Solvent	M. p., °C.	Action with H_2O
1	Acetate	Needles	Chloroform	63–64	Unstable
2	Lactate	Plates	Dil. CH_3OH	134.5	Stable
3	Oxalate	Plates	Ether-alcohol	167	Unstable
4	Benzoate	Needles	Ether-gasolene	72.5	Unstable

TABLE II

ANALYTICAL DATA

	Formula	Calculated for, %		Found, %
1	$C_{12}H_{20}O_2N_2$	CH_3COOH	26.8	27.1
2	$C_{13}H_{23}O_3N_2$	N	11.03	11.44
3	$C_{12}H_{18}O_4N_2$	$(COOH)_2$	21.50	21.53
4	$C_{17}H_{22}O_2N_2$	C_6H_5COOH	42.66	42.71

***m*-Nitrobenzaldehyde-*p*-cymylhydrazine-2**, $C_{10}H_{13}NHN{:}CHC_6H_4NO_2$.—Two grams of the aldehyde was dissolved in a very little petroleum ether–alcohol (1–1) and mixed with 5 g. of cymylhydrazine in 5 cc. of petroleum ether. A bright red precipitate formed at once. The product crystallizes beautifully from glacial acetic acid, alcohol or benzene, hot solutions on cooling giving abundant yields of rectangular prisms which melt at 143°. The crystals are very rich red, though yellow by transmitted light. Ether or acetone solutions may be precipitated by heptane. The compound is stable toward hot water.

Anal. Calcd. for $C_{17}H_{19}O_2N_3$: N, 14.14. Found: 14.23.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY OF THE
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA

ALVIN S. WHEELER
THOS. L. KING

RECEIVED NOVEMBER 28, 1930
PUBLISHED FEBRUARY 9, 1931

Homochromanone.[1,2]—Since phenoxyacetic and β-phenoxypropionic acids can be converted by loss of water into coumaranone[3] and chromanone,[4] respectively, it seemed likely that homochromanone could be obtained in a similar manner from γ-phenoxybutyric acid. It was found in this investigation that γ-phenoxybutyric acid did yield homochromanone, although, as might have been expected, the formation of the 7-membered ring did not take place as smoothly as that of the 6-membered ring in chromanone. In fact, the yields were so poor that proper purification of the product was impossible due to the small quantity obtained.

Attempts to dehydrate y-phenoxybutyric acid with phosphorus pentachloride and with thionyl chloride were unsuccessful. Treatment of the acid with thionyl chloride and then with anhydrous aluminum chloride yielded no homochromanone. It was found that the best results were obtained by dehydrating the acid in small portions (1g.) with phosphorus pentoxide.

Although no pure homochromanone was obtained, the semicarbazone and oxime were prepared and purified.

Homochromanone.—One gram of y-phenoxybutyric acid dissolved in 15 cc. of benzene was treated with 1 g. of phosphorus pentoxide following the method described by one of us[4]" for the preparation of chromanone. On evaporation of the benzene a few drops of a lemon-yellow, highly refracting oil remained. Attempts to induce crystallization were unsuccessful, and even after combining the product from several runs, not enough was obtained to carry out a distillation. The oil was readily soluble in ether, benzene, petroleum ether and alcohol. A drop dissolved in concd. sulfuric acid gave a red solution on warming.

Semicarbazone.—This was prepared in the same manner as chromanone semicarbazone. It crystallizes from alcohol in white needles, m.p. 228–229° (uncorr.).

Anal. (Kjeldahl). Subs., 0.0980, 0.2231: HCl (0.0969 N), 14, 31.04 cc. Calcd. for $C_{11}H_{13}O_2N_3$: N, 19.2. Found: 19.4, 18.9.

Oxime.—This was prepared in the same manner as chromanone oxime. It crystallizes from petroleum ether in white plates, m. p. 99°.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

S. G. POWELL
LUCILE ANDERSON

RECEIVED DECEMBER 22, 1930
PUBLISHED FEBRUARY 9, 1931

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[1] Presented at the Cincinnati meeting of the American Chemical Society, September, 1930.

[2] This paper is taken from a portion of a thesis submitted by Lucile Anderson in partial fulfilment of the requirements for the degree of Master of Science.

[3] Stoermer and Bartsch, *Ber.*, 33, 3175 (1900).

[4] (a) Powell, THIS JOURNAL, 45, 2708 (1923); (b) Arndt and Källner, Ber., 57B, 202 (1924).

COMMUNICATIONS TO THE EDITOR

COAGULATION OF FERRIC OXIDE HYDROSOLS

Sir:

In a recent communication [THIS JOURNAL, 52, 4170 (1930)] N. R. Dhar suggests that "the results of Judd and Sorum [THIS JOURNAL, **52,** 2598 (1930)] are not in agreement with previous work and need confirmation." The "previous work" referred to is that of Dhar and his collaborators, particularly that reported by Dhar and Gore [J. Indian Chem. *Soc.*, *6*, 31 (1929)], in which the conclusion is drawn that "even highly purified sols of ferric hydroxide containing very small amounts of chloride ion follow the general rule that the greater the concentration of the sol the greater is the amount of electrolyte necessary for coagulation irrespective of the valency of the coagulating ion."

If the two papers in question are compared it will be obvious that Dhar's own results, when properly analyzed, fall in line with the very conclusion with which he seems to take issue. Figure 4, page 2601, in the paper by Sorum and Judd represents graphically the influence of the addition of ferric chloride on flocculation values. If the increase in chloride content, as represented by millimoles of ferric chloride added per liter, is greater than 0.0095 g. per liter, the sol behaves as did Dhar's, i. e., the flocculation value with sodium chloride increases with increased sol concentration. It is only when the added chloride is less than 0.0095 g. per liter that the sol follows the Burton–Bishop rule. An examination of Dhar's results will show that in no case is the chloride content of the purified sol anywhere nearly as low as that represented by the above figure. The best figure is 0.0936 g. per liter, ten times the critical value represented in Figure 4 cited above. As such it would seem that Dhar's criticism is not very well founded.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON. WISCONSIN

C. HARVEY SORUM

RECEIVED DECEMBER 5, 1930
PUBLISHED FEBRUARY 9, 1931

DERIVATIVES OF OPTICALLY ACTIVE TRIARYLCARBINOLS AND THEIR HALOCHROMIC SALTS

Sir:

In a recent article published in the Proceedings of the National Academy of *Sciences* [**16,** 215 (1930)], I described a method for preparing an optically active triarylcarbinol in the form of its thioglycolic acid derivative. *l*-Phenylbiphenyl-α-naphthylmethylthioglycolic acid, $(C_6H_5C_6H_4)(C_{10}H_7)$-$(C_6H_5)C$—$SCH_2COOH$ (hereafter designated as **A**), has the following specific rotation in carbon tetrachloride, $[\alpha]^{20}_{D}$ $-13.63°$. Experiments with this substance show that it forms halochromic salts. Concentrated sulfuric acid, perchloric acid, and mercuric chloride unite with it, forming deep violet halochromic compounds, which on pouring into ice water yield the carbinol, $(C_6H_5C_6H_4)(C_{10}H_7)(C_6H_5)C—OH$, in its optically inactive form. A solution of titanium tetrachloride in chloroform when added to a chloroform solution of **A** produces a deep violet halochromic salt which on decomposition with water yields A in its racemic form. However, when a solution of ferric chloride in glacial acetic acid is added to a chloroform solution of A, the deep violet halochromic salt so formed, on pouring into ice water, produces the original *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid with no racemization.

The fact that the halochromic salt with ferric chloride on decomposition with water gives the original optically active thioglycolic acid derivative with no change in specific rotation is compelling evidence against quinoid formulation for the explanation of color. A detailed account of these experiments will be published shortly.

FRICK CHEMICAL LABORATORY
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PRINCETON, NEW JERSEY

EVERETT S. WALLIS

RECEIVED JANUARY 23, 1931
PUBLISHED FEBRUARY 9, 1931

THE VELOCITY OF ADSORPTION PROCESSES AND THE PROBLEM OF PROMOTER ACTION

Sir:

In a recent note [THIS JOURNAL, 52, 5298 (1930)] and in greater detail in a communication to the February issue of THIS JOURNAL, the data relative to the concept of activation energy of adsorption processes has been indicated. In these contributions it was emphasized that the magnitude of the activation energy and, hence, of the velocity of adsorption at a given temperature, is determined not only by the adsorption process in question but also by the nature of the surface area on which the process occurs. We can now record some striking examples of this view which bear fundamentally on the problem of promoter action in catalysis. We have found that on an active manganous oxide catalyst hydrogen is adsorbed immeasurably slowly at 0 and 100°. At 184° the initial rate of absorption in a given adsorption system was 8 mm. per hour. At 305" the velocity of adsorption had risen to 78 mm. per hour, which corresponds to an activation energy in the neighborhood of 10,000 calories. The hydrogen was reversibly adsorbed since it could be recovered quantitatively by evacuation at higher temperatures. To compare these data with a promoted catalyst we have now studied a manganous oxide–chromium oxide catalyst. This again shows an extremely slow rate of adsorption at 0°, but at 184°, in a system comparable to that used with manganous oxide, the velocity of adsorption had risen to approximately 100 mm. per *minute.* The velocity of adsorption had thus increased about 700-fold by reason of the promoter action of the chromium oxide. The promoted catalyst also showed a much increased adsorptive capacity per gram. The gas was reversibly adsorbed. It is evident, therefore, that in considering the mechanism of promoter action consideration must be given not only to extension of surface but also to the velocities with which the activating adsorptions occur.

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HUGH S. TAYLOR
ARTHUR T. WILLIAMSON

RECEIVED JANUARY 30, 1931
PUBLISHED FEBRUARY 9, 1931

NEW BOOKS

Die Bedeutung der wissenschaftlichen Tätigkeit Friedrich Wöhlers für die Entwicklung der deutschen chemischen Industrie. (The Importance of Friedrich Wöhler's Scientific Achievements in Developing German Chemical Industry.) By Dr. TH. KUNZMANN. **Verlag Chemie, G. m. b. H., Berlin W 10, Germany, 1930. 90** pp. **15.5 × 23.5 cm. Price, unbound, RM. 4.**

Within the space of ninety pages the author includes those discoveries by Wohler that led to important technical processes, as well as his purely scientific achievements. He presents in thirteen chapters an admirable survey of all this great pioneer did, beginning with a list of Wohler's papers, **223** in all, upon 160 inorganic, 54 organic and 9 biochemical subjects. Those were days when a man was a general practitioner, unconfined to a special field but roaming at will and able to say truthfully, "I am a chemist." In the second chapter is Wohler's biography and in the next four are such technically important discoveries as the isolation of aluminum in 1827, contact production of sulfuric acid in **1852,** explanation of the nature of calcium carbide with suggestions as to its use in 1862, and experiments upon titanium in 1849. Fourteen additional inorganic researches of technical significance appear in the eighth chapter, among the number being the extraction of phosphorus, refining of antimony and oxidation of ammonia.

No book about Wohler would be complete without mention of his announcement in **1828** of the synthesis of urea. In the ninth chapter the author takes up this discovery that has overshadowed much of Wohler's other work. The birth of modern synthetic chemistry dates from this epoch-making experiment that spurred chemists to attempt similar syntheses. The two following chapters call attention to other organic researches by Wohler, such as those upon alkaloids and quinone, the latter leading to the preparation of hydroquinone and quinhydrone. In its subsequent development quinone chemistry has proved a fruitful field of research. His organic experiments led Wohler to devise several ingenious methods, for example, the use of the sealed tube.

The twelfth chapter emphasizes Wöhler's eminence as a teacher. His laboratory was the Mecca of many students of chemistry. The analytical skill he had mastered under Berzelius he insisted upon imparting to his followers and his laboratory became renowned for the exactness of the work done there. Many of his students afterward acquired fame both in academic and in technical circles, among the number being Fittig, Kolbe, Beilstein and many others.

That unique episode in the history of chemistry, namely, the collaboration of Wohler and Liebig, occupies the thirteenth chapter. Working independently, each in his own laboratory, they completed thirteen valuable pieces of work, some of which have become classical examples of chemical research. Three of these researches, namely, those upon the radical of benzoic acid, emulsin, and uric acid, are considered at length. Possibly the general adoption of this method of working might result in fewer but better papers and prevent the waste of many splendid trees.

In the concluding chapter the author summarizes Wohler's chemical career and closes with an appendix upon the influence of the scientific labors of Wohler, Liebig and Schönbein in developing German chemical industry.

W. H. WARREN

Ostwald-Luther. Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen. (Physico-Chemical Measurements.) Edited by C. DRUCKER. Fifth, revised edition. Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany, 1931. xix + 979 pp. 630 figs. 16 × 23.5 cm. Price, unbound, RM. 49; bound, RM. 52.

Only a detailed comparison of the fifth with the fourth edition could make clear the extent of the improvements effected by this latest revision. The text has grown by one hundred and fifty pages, the cuts by seventy. A wealth of references has been added, with adequate recognition of English and American investigators, while increased emphasis is laid upon recent technical books and critical summaries. Each cut is now provided with a suitable legend—an overdue concession to the inexpert. Among the new topics may be mentioned electroplating, preparation of metallic wires, the sputtering of metals, diffusion electrodes, glass membrane electrodes, magnetic measurements. While minor changes appear everywhere, the sections on calorimetry, conductivity, electron tube hookups, x-rays, radioactivity, electrometric titration and electrical temperature measurements have gained the most in usefulness. The alumni of the Physikalisch-Chemisches Institut in Leipzig may feel a passing regret over the disappearance of the course of laboratory exercises once given there. By way of compensation, however, the more important (German) laboratory manuals are listed.

From the very beginnings of modern physical chemistry, "Ostwald-Luther" has embodied and furthered its progress. The latest edition sets a standard of excellence which will be hard indeed to surpass.

G. S. FORBES

Geochemie in ausgewählten Kapiteln. (Selected Chapters in Geochemistry.) By W. J. VERNADSKY. Authorized translation from the Russian, by Dr. E. KORDES, Mineralogical Institute of the University of Leipzig. Akademische Verlagsgesellschaft m.b.H., Schlossgasse 9, Leipzig C 1, Germany, 1930. xii + 370 pp. 15.5 X 23.5 cm. Price, unbound, RM. 23; bound, RM. 25.

The term "geochemistry" is commonly used in two different meanings. Its first and more logical meaning is "chemistry of the Earth," with a capital E; that is, the chemistry of our planet considered as an object, in the sense in which we would speak of the chemistry of an orange or of a micro-organism. Its second and more usual meaning is "chemistry of earth" with a small e, that is, the chemistry of minerals, rocks, and soils, in which sense it is essentially a branch of general chemistry, and consists of facts that could be used, without modification, by the inhabitants of any other planet. Vernadsky's "Geochemistry" is about eighty per cent. of the first kind and twenty of the second. Twenty per cent. is no more than is necessary for a clear understanding of the other eighty, particularly if such reference works as Mellor's Volume VI or Doelter's "Handbuch" are not available. Furthermore, the inclusion of this twenty makes possible the presentation in condensed form of some of the valuable data and conclusions drawn from the experimental researches of the author, who has been a life-time investigator in mineral chemistry, and whose work was long ago recognized by his election as a member of the Russian Academy. A distinguishing feature of the strictly geochemical part of the book is the emphasis placed upon the relations of the activity of living organisms, including Man himself, to the chemistry of the Earth's surface shell. This aspect of the subject has received relatively little attention from earlier writers.

The German translator has confined himself to making a faithful transcript of the author's ideas, basing his translation on the Russian edition of 1927, which in turn was an enlargement of the original French edition of 1924. At the same time the author has rewritten certain chapters, where new experimental knowledge has made a revision desirable.

ROBERT B. SOSMAN

Stereochemie. (Stereochemistry.) By GEORG WITTIG, Lecturer at the University of Marburg. Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany, 1930. xi + 388 pp. 127 figs. 16 X 23.5 cm. Price, unbound, M. 23; bound, M. 25.

Stereochemistry has considerably expanded during the past few years, not only in the amount of its data but in its scope, and from various sides so much progress has been made that the real ultimate goal—to specify in absolute units the spatial distribution of atoms within molecules—is now clearly visible. This subject is no longer exclusively concerned with certain particular kinds of isomerism, and whatever one's special field as a student or investigator in organic chemistry may be, there are some topics of stereochemistry concerning which it is necessary to be informed.

The problem of finding the needed information now presents no difficulties. For a clear and concise statement of the current status of any particular problem, or for a well-ordered and thoroughly readable account of the entire field, one has only to turn to Dr. Wittig's book. Specialists in stereochemistry may find his discussion of some of their favorite topics disappointingly brief, but if there is any error of judgment in this respect, the error certainly lies in the right direction so far as the general utility of the book is concerned, and for those who are interested in details, copious references to the original literature are supplied. The only topics that have received less emphasis than their importance warrants are ones such as the stereochemistry of sugars that have already been recently reviewed in other books. On the other hand, half the book is devoted to the stereochemistry of other elements than carbon and nitrogen, stereochemistry and crystal structure, and stereochemistry and reaction kinetics, and under the second of these headings one finds discussions of the hypothesis of Reis and Weissenberg, the spatial forms of aliphatic chains, the polymorphism of organic compounds, and the stereochemistry of high polymers. The text is copiously illustrated with excellent figures. The printing is well done and there is a good index. Every organic chemist, no matter what his special interests may be, will find it worth while to own a copy of this book.

WALLACE H. CAROTHERS

Fundamentals of Organic Chemistry. BY HARRY F. LEWIS, Professor of Organic Chemistry, Institute of Paper Chemistry, Appleton, Wisconsin. International Chemical Series, James F. Norris, Consulting Editor. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1930. viii + 390 pp. 28 figs. 14.5 X 21 cm. Price, $2.75.

As stated in the introduction, this book is intended to remedy the lack of a recent American text built specifically upon the "Atomic Linking Theory." The various classes of compounds are considered in terms of functional groups, *e.* g., the reactions of an acid are presented as the resultant of the following groups, —C—C, C—H, C=O in presence of OH and OH in presence of C=O.

The book is written in three parts: Part I, The Petroleum Hydrocarbons and their Monosubstitution Products; Part II, The Polysubstitution Products of the Petroleum Hydrocarbons; and Part III, The Ring Compounds.

Emphasis has been placed upon the development made in organic chemistry since the World War, many modern processes being described. There is a goodly assortment of questions and problems and also, at the end of several chapters, references are given for outside reading. However, some of these references would be rather heavy reading for a student in elementary organic chemistry, e. g., "Proteins and the Theory of Colloidal Behavior" by Loeb, "The Physical Chemistry of Proteins" by Robertson, and "Recent Advances in Organic Chemistry" by Stewart.

On the whole, this book should prove to be a usable and interesting text, especially for those teachers interested in the "Atomic Linkage" presentation of organic chemistry.

BEN B. CORSON

Handbuch der biologischen Arbeitsmethoden. (Handbook of Biological Methods.) Edited by Professor Dr. EMIL ABDERHALDEN. Section I. Chemical Methods, Part 2, 2d half, Number 6. Die Verseifung. (Saponification.) By FRANZ BACHÉR, Rostock. Urban and Schwarzenberg, Friedrichstrasse 105b, Berlin N 24, Germany, 1930. 294 pp. 17.5 × 25.5 cm. Price, M. 16.

The present number of Abderhalden's comprehensive "handbook" deals with the saponification of all common types of derivatives of organic acids: anhydrides, chlorides, esters, lactones, nitriles, amides and anilides. It is by far the most extensive and detailed treatment of the subject that is available. By discussion of underlying principles and by very many carefully selected examples the author indicates the most promising methods for solving difficult problems in saponification, like the partial hydrolysis of derivatives of polybasic acids or of polyacid alcohols; the saponification of optically active esters and amides, of esters and nitriles of β-ketonic acids and other similarly unstable compounds, and of substances in which there is a great hindrance to hydrolysis.

Organic chemists as well as the biochemists for whom, presumably, it was primarily prepared will find in this excellent treatise much time and patience saving material.

E. P. KOHLER

BOOKS RECEIVED

December 15, 1930—January 31, 1931

WALTER L. BADGER AND WARREN L. MCCABE. "Elements of Chemical Engineering." Introduction by Arthur D. Little. McGraw-Hill Book Company, Inc., New York. 625 pp. $5.00.

J. F. T. BERLINER. "Potash Bibliography to 1928 (Annotated)." Review and Compilation of Technical Literature on Potash Salts (Including the Alunites) and their Foreign Occurrences. U. S. Department of Commerce, Bureau of Mines, Bulletin 327. Government Printing Office, Washington, D. C. From Superintendent of Documents. 578 pp. $0.90.

Günther Bugge. "Das Buch der grossen Chemiker. Von Liebig bis Arrhenius." Vol. II Verlag Chemie, G. m. b. H., Berlin W 10. 559 pp. M. 32.

A Frederick Collins "Experimental Chemistry, being a Series of Simple and Spectacular Experiments in Chemistry, together with Some Home-made Chemical Apparatus." Illustrated by the Author. D. Appleton and Company, New York. 276 pp. $2.00.

P A. M. Dirac. "The Principles of Quantum Mechanics." The Oxford University Press, 114 Fifth Avenue, New York 257 pp.

K. Fajans and J. Wüst. "A Textbook of Practical Physical Chemistry." Translated from the German by Bryan Topley. Preface by F. G. Donnan. E. P. Dutton, Inc., 286–302 Fourth Ave., New York. 233 pp. $4.95.

Fritz Feigl. "Qualitative Analyse mit Hilfe von Tüpfelreaktionen. Theoretische Grundlagen und praktische Ausfuhrung." Akademische Verlagsgesellschaft m. b. H., Leipzig. 387 pp. RM. 26.40, unbound; Rm. 28, bound.

"Gmelins Handbuch der anorganischen Chemie." Eighth Edition. System-Number 59: Eisen. Teil A, Lieferung 3. Herausgegeben von der Deutschen Chemischen Gesellschaft. Verlag Chemie, G. m. b. H., Berlin W 10. 274 pp. RM. 32 to subscribers

Wo. Ostwald, Editor. "Organische Chemie und Kolloidchemie." Sonderheft der Kolloid-Zeitschrift. Band LIII, Heft 1. Haupt-vortrage gehalten auf der VIII Hauptversammlung der Kolloid-Gesellschaft im Frankfurt a. M., vom 9–11 Juni, 1930. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz. 124 pp. RM. 8, unbound.

K. A. Redlich, J. C. Breinl and H. Tropsch, Editors. "Entstehung, Veredlung und Verwertung der Kohle." Vortrage gehalten an der Technischen Hochschule in Prag. Verlag von Gebrüder Borntraeger, W 35 Schoneberger Ufer 12a, Berlin. 359 pp. M. 30, unbound; M. 33, bound.

Fritz Reiche "The Quantum Theory." Revised Edition. Translated by H. S. Hatfield and Henry L. Brose. E. P. Dutton and Co., Inc., 286–302 Fourth Ave., New York. 218 pp. $2.10.

Hugh S. Taylor, Editor. "A Treatise on Physical Chemistry. A Cooperative Effort by a Group of Physical Chemists." D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York. Two volumes, illustrated. Vol. I, 852 pp. Vol. II, 914 pp. Price, set, $15.00.

Maximilian Toch. "The Protection and Decoration of Concrete." D. Van Nostrand Co., Inc., 250 Fourth Ave., New York. 54 pp. $2.00.

W. Ewart Williams. "Applications of Interferometry." Preface by O. W. Richardson. E. P. Dutton and Co., Inc., 286–302 Fourth Ave., New York. 104 pp. $0.85.

Mihai Zapan. Thèses, presentees a la Faculté des Sciences de l'Université de Paris, pour obtenir le Grade de Docteur es-Sciences Physiques. "Sur la chloruration et la bromuration catalytique des gaz riches en hydrocarbures méthaniques." Impressions Industrielles (G. de Zerman), 25 Rue Turgat, Paris. 100 pp.

"Abridged Scientific Publications from the Kodak Research Laboratories." Volume VIII, 1929. Published by the Eastman Kodak Company, Rochester, New York. 271 pp.

"A. S. T. M. Standards, 1930." Issued triennially. Published by the American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa. Part I, Metals, 1000 pp. Part II, Non-Metallic Materials, 1214 pp. Each part, cloth, $7.50; both parts, $14.00.

"Cellulose." February, 1931, Announcement Issue. Vol. 1, No. 1. The Cellulose Publishing Co., Publishers, 114 East 32d St., New York. 42 pp. $3.00 a year; 35 cents a copy.

"59 Vortrage (mit Diskussionen) darunter 13 zusammenfassende Vortrage über das Hauptthema: Spektroskopie und Molekelbau." XXXV Hauptversammlung der Deutschen Bunsen-Gesellschaft für Angewandte Physikalische Chemie E V., vom 28 Mai bis 1 Juni, 1930, zu Heidelberg. Verlag Chemie G. m. b. H., Berlin W 10. 259 pp. RM. 12, unbound.

I. G. Farbenindustrie Aktiengesellschaft. "Veriiffentlichungen des Wissenschaftlichen Zentral-Laboratoriums der Photographischen Abteilung—AGFA." Volume I. Verlag von S. Hirzel, Königstrasse 2, Leipzig, Germany. 155 pp. RM. 10.

The Journal of the
American Chemical Society

VOL. 53 MARCH, 1931 NO. 3

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

THE MEASUREMENT OF THE HYDROGEN-ION CONCENTRATION IN UNBUFFERED SOLUTIONS.

II. APPLICATION OF THE HYDROGEN ELECTRODE

BY I. M. KOLTHOFF AND TOHRU KAMEDA[1]

RECEIVED JUNE 9, 1930 PUBLISHED MARCH 6, 1931

It has already been shown[2] that a platinized electrode in a hydrogen atmosphere adsorbs the cation or base from a salt or basic solution, thus yielding a more acid solution in the cell than before the treatment with hydrogen. All experiments described in the former paper have been repeated in a nitrogen atmosphere. There was no adsorption of cation or anion in any case. This proves definitely that the absorbent property of platinized platinum for strong electrolytes is a function of the electrode property (hydrogen or oxygen) of the noble metal (Frumkin).

The fact that the ordinary type of platinized hydrogen electrode adsorbs cations from a solution forms a serious objection to its use for PH measurements in unbuffered solutions. In order to overcome this change of the reaction in a slightly buffered or unbuffered solution, it is evident that the coat of platinum has to be as thin as possible.

H. T. Beans and L. P. Hammett[3] in an important paper arrived at a similar conclusion. They pointed out that the bare platinum electrode is a poor catalyst for the reaction $H_2 \rightleftarrows 2H^+ + 2e$, but that bright metallic deposits of platinum prepared electrolytically act catalytically for the hydrogen-ion reaction, and their life, while not as long as that of platinum black, is sufficient to make their use as hydrogen electrodes possible. Beans and Hammett's results were in the main confirmed by the authors, though there is one important difference between their observations of the adsorbent properties of platinized platinum and those of the authors, which can be attributed to the fact that this property of the electrode is a function of its gas charge. Acids which are adsorbed by the air electrode

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[1] From the experimental part of a thesis submitted by T. Kameda to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] I. M. Kolthoff and T. Kameda, THIS JOURNAL, 51, 2888 (1929)

[3] H. T. Beans and L. P. Hammett, *ibid.*, 47,1215 (1925).

are not adsorbed by the hydrogen electrode and, therefore, can be removed from the electrode by washing out in a hydrogen atmosphere with water. This point is very important with regard to the preparation of an electrode suitable for the measurement of *PH* in unbuffered solutions. Many attempts, a discussion of which has been given in the thesis of T. Kameda,[1] have been made to prepare such an electrode. Finally, it was decided to cover platinum or gold with a bright layer of platinum, as has been suggested already by Beans and Hammett.[3] However, the procedure followed was different from that given by the authors mentioned, since it has been found that adsorbed acid can be removed easily by washing in a hydrogen atmosphere.

Materials

Chloroplatinic Acid.—Pure platinum was prepared according to the directions of Wichers.[4] The metal was dissolved in aqua regia, evaporated several times with hydrochloric acid and then several times with water. This residue was taken up in water so that the resulting solution contained about 2% of platinum as chloroplatinic acid.

Hydrogen.—This was taken from a commercial cylinder and carefully purified by passing through a wash-bottle containing alkaline permanganate over a column of pure copper wire gauze electrically heated at 450–500° and various wash-bottles.

Water.—Conductivity water was distilled over extremely dilute sulfuric acid in order to remove traces of basic impurities, then twice without any addition and finally in a quartz apparatus with condenser. The distillate was collected in a quartz container and protected from contamination by the atmosphere. Usually the final distillate was used the same day as prepared. As will be shown in another paper, this water when made carbon dioxide free has a PH of 7.0 to 7.05.

Potassium Chloride and Potassium Sulfate.—C. P. products were twice recrystallized from water and the crystals ignited for two hours in an electric furnace at 600°.

Ammonium Chloride.—A C. P. product was twice recrystallized from water and dried in a desiccator.

Zinc Sulfate.—A C. P. product was recrystallized seven times from water (for details compare next paper) and dried over deliquescent sodium bromide at a temperature below 23° until the weight was constant.

The Hydrogen Electrode Adapted for Unbuffered Solutions.—A diagram of the cell finally used is given in Fig. 1. All glass parts were made of pyrex glass. A platinum and a gold wire, both about 3 cm. long and 1 mm. thick, were used as electrodes. The wires were fused through a pyrex glass tube and sealed to a thin platinum wire which made the connection with a copper wire. These glass tubes were ground air tight into the upper part of the glass cell. In all cases it was found that the platinum and gold electrodes gave identical readings within 0.3 of a millivolt. It is recommended that platinum wire be used, as it is much easier to handle than the soft gold. Before platinization the electrodes are

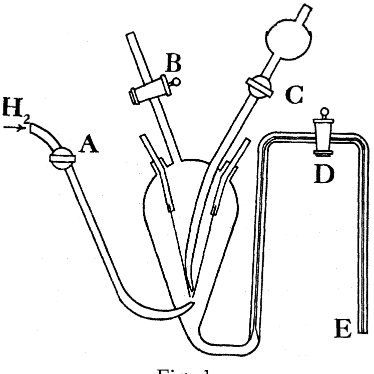

Fig. 1.

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[4] Wichers, THIS JOURNAL, 43, 1268 (1921).

treated with a solution of potassium dichromate in strong sulfuric acid, washed with water and heated to dull redness. The plating bath contained a solution of pure chloroplatinic acid of a concentration corresponding to 2% platinum. By electrolyzing for two minutes at a current strength of 20 milliamperes, both electrodes are covered with a bright layer of platinum. The current density can be varied within wide limits. Good results are obtained at a current strength between 5 and 30 milliamperes. After the plating, the electrodes are washed well with water and then placed in the electrode cell, which is filled with conductivity water through which hydrogen has been passed for twenty minutes. The passage of hydrogen is continued for about thirty minutes, then the water is forced out of the cell in the hydrogen current. The solution to be tested is washed in hydrogen and introduced in a continuous stream which enters through A by opening stopcock C, closing D and opening B. After a few minutes the solution is again removed and the washing of the electrode in hydrogen is repeated several times. Finally the cell is partly filled with the solution so that about 2 cm. of the electrodes are covered, when the solution is not stirred. The passage of hydrogen is still continued with the stopcocks A and B open. Before taking a reading B is closed, then A, whereupon D is opened. Then the end E of the capillary tube is dipped into a saturated potassium chloride solution contained in a cell as shown in Fig. 2.

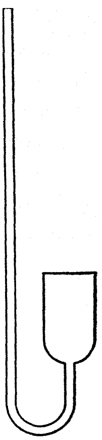

Fig. 2.

The electrodes are easily poisoned in unbuffered solutions. After each set of measurements the electrodes have to be cleaned, replated and treated as described above. Under these conditions reproducible results are obtained even in unbuffered solutions.

Results.—The most difficult problem, of course, is the PH measurement in an unbuffered solution such as potassium chloride. A 0.05 molar solution of this salt was used.

It was not possible to obtain a constant e. m. f.; in the beginning it increased (corresponding to an increase in PH), then it reached a maximum and remained constant for fifteen to thirty minutes, after which the values dropped slowly. Some results are given in the following table.

PH OF 0.05 MOLAR POTASSIUM CHLORIDE WITH THE HYDROGEN ELECTRODE AT 25°

Time in minutes....	15	30	45	55	90
PH..	6.66	6.76	6.75	6.73	6.53

Electrodes Replatinized

Time in minutes....	15	30	40	50	70
PH...............	6.72	6.77	6.77	6.76	6.73

These measurements have been repeated eight times. In all cases a maximum in PH was reached after hydrogen had been passed through for twenty to thirty minutes. If the cell was refilled with fresh potassium chloride solution after one set of measurements, no good results were obtained, the *PH* indicated being much too low. Removing the film of platinum with aqua regia, igniting and replating the electrode was necessary. The *PH* of the potassium chloride solution was also determined colorimetrically with brom thymol blue as indicator (for technique compare next paper). In this way a value of 6.77 was found, the latter being in close agreement with the reading of the hydrogen electrode.

In 0.05 molar potassium sulfate solutions a PH of 7.4 ± 0.05 was found potentiometrically.

Finally, many measurements have been made in solutions of ammonium chloride and of zinc sulfate. The e. m. f. remains constant over a much longer period of time than in the case of potassium chloride solutions and in addition the solutions can be renewed a few times before replating the electrode.

Some results are reported in the following table. The PH values have also been determined colorimetrically with adjusted methyl red as indicator (for technique see next paper). Methyl red is of special utility here on account of its negligibly small salt error.

PH IN AMMONIUM CHLORIDE AND ZINC SULFATE

Solution used	PH (H_2 electrode)	PH (color, methyl red)
0.25 Molar NH_4Cl	4.97	4.96
.01 Molar $ZnSO_4$	6.00	6.00
.02 Molar $ZnSO_4$	5.89	5.90
.05 Molar $ZnSO_4$	5.76	5.77
.1 Molar $ZnSO_4$	5.67	5.66

In more concentrated solutions of zinc sulfate the measurements with the hydrogen electrode were not so well reproducible. Quite generally it may be mentioned that in this tedious work irregularities occur once in a while. These may be due to inadequate platinization, but also it should be remembered that unbuffered solutions like those of neutral salts are very sensitive toward changes of their reaction.

Summary

Use is made of the fact that acid adsorbed by platinum can be removed by washing with water in a hydrogen atmosphere. Directions have been given for the preparation of an electrode coated with a bright layer of platinum, the use of which yields satisfactory results in the measurement of PH in unbuffered or slightly buffered solutions. The electrode is easily poisoned and cleaning and replatinizing are often required, but reproducible results can be obtained even in solutions of potassium chloride.

MINNEAPOLIS, MINNESOTA

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

THE MEASUREMENT OF THE HYDROGEN-ION CONCENTRATION IN UNBUFFERED SOLUTIONS.
III. THE COLORIMETRIC METHOD

BY I. M. KOLTHOFF AND TOHRU KAMEDA[1]

RECEIVED JUNE 9, 1930 PUBLISHED MARCH 6, 1931

I. Acid–base indicators are substances with a weak acidic or basic character and therefore they have a tendency to change the P_H when added to a slightly buffered or unbuffered solution. As the molecular concentration of indicators in colorimetric work is of the order of 10^{-5} or smaller, the "acid" or "base" error will only be noticeable in solutions with extremely slight buffer action. Large errors, however, may occur when the P_H of pure water or solutions of neutral salts in water or extremely dilute solutions of acids and bases have to be measured. I. M. Kolthoff,[2] for example, found that 0.1 cc. of a 0.04% solution of methyl red added to 10 cc. of water (P_H 7.0) gave a color corresponding to a P_H of 5.1. He has already pointed out that in the measurement of P_H in slightly buffered solutions, reliable results can only be obtained if the indicator solution added has the same P_H as the unknown. Edna H. Fawcett and S. F. Acree,[3] who recently published extensive papers on the colorimetric measurement of P_H in unbuffered solutions, call these indicator solutions adjusted or isohydric.

In unknown cases mixtures of the two forms of the indicator in different ratio must be used. If different amounts of the mixture added to the unknown give the same P_H, it is isohydric with the latter. This has been pointed out already by W. H. Pierre and J. F. Fudge,[4] and especially emphasized by Fawcett and Acree.[3]

The color of the indicator in the unbuffered solution is compared with that of the same mixture in an ordinary buffer solution. As the ionic strength of the two may be quite different, a correction must be applied for the difference in activity of the indicator ions in both solutions.[5]

II. Preparation of Adjusted Indicator Solutions.—For the preparation of adjusted solutions, H. T. Stern[6] titrated the indicators with sodium hydroxide and determined the P_H with the quinhydrone electrode. It is

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[1] From the experimental part of a thesis submitted by T. Kameda to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] I. M. Kolthoff, *Biochem. Z.*, 168, 110 (1926).

[3] E. H. Fawcett and S. F. Acree, *J. Bact.*, 17, 163 (1929); *Ind. Eng. Chem., Anal Ed.*, 2, 78 (1930).

[4] W. H. Pierre and J. F. Fudge, THIS JOURNAL, 50, 1254 (1928).

[5] *Cf.* I. M. Kolthoff, *J. Phys. Chem.*, 32, 1820 (1928).

[6] H. T. Stem. *J. Biol. Chem.*, 65, 675 (1925).

claimed that the readings are accurate to within about 0.2 in YH, Pierre and Fudge[4] used a similar technique; however, the results described by these authors are not very convincing. In their table[7] a close agreement between the reading with the hydrogen electrode and the colorimetric ''varying drop method is shown. This agreement, however, is more or less illusory as they neglect the difference in ionic strength between the unknown and the buffer. The correction may amount to 0.2–0.3 in PH.

Fawcett and Acree[3] prepared series of adjusted indicators of known PH more in an empirical way, by noticing the change in color upon addition of an equal volume of a very dilute buffer solution. As a matter of fact, it is not very important to know the PH of the indicator mixture with a high degree of accuracy. As the PH of the solution to be tested is not known, different indicator mixtures must be tried, until one is found which gives the same reading after addition of different amounts of indicator. The color is then compared with that of the same amount of indicator in buffer solutions of known PH. More important is the use of pure indicators in this type of work. Most commercial products show quite a variation in their composition. Therefore, the authors have tried to prepare pure samples of indicators; their purity was tested by a conductimetric titration with sodium hydroxide. If a solution of a sulfonephthalein is titrated, the conductivity drops as in the titration of any strong acid. After the neutralization of the sulfonic group, the conductivity increases and a second break in the conductivity line occurs after the neutralization of the phenol group. Upon further addition of sodium hydroxide, there is a much stronger increase in conductivity. In the titration of phenolphthalein only one break in the conductivity line occurs after addition of two equivalents of sodium hydroxide (neutralization of carboxyl and phenolic group). In the neutralization of methyl red only one break can occur after addition of one equivalent of base.

If pure indicators are available, the composition of mixtures of a definite *PH* can be calculated by means of the equation

$$\frac{[HI^-]}{[I^-]} \quad \frac{(H^+)}{K_1}$$

The most reliable data of the ionization constant K_1 of the indicators have been collected by Kolthoff[S] and the authors have used these figures in their computation.

Indicators Used

Brom Thymol Blue.—A product of Scheting–Kahlbaum was recrystallized from benzene: 1.5% was insoluble; this residue was sodium chloride. The crystals were dried at 190° to remove all water. The conductimetric titration showed that this product was quite pure. The data obtained are summarized in the table.

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[7] Ref. 4, p. 1260.

[8] I. M. Kolthoff, J. Phys. Chem., 34, 1466 (1930).

Phenol Red.—Commercial products are usually impure. According to W. R. Orndorff and F. W. Sherwood,[9] phenol red is usually contaminated by a dyestuff with weak acid character, which is insoluble in sodium bicarbonate. Therefore, the crude product can be purified by dissolving it in sodium bicarbonate solution and acidifying the filtrate with hydrochloric acid. The phenol red is collected and dried at 130". A product of Schering–Kahlbaum was still impure after this treatment. Further crystallization from acetic acid is necessary to obtain it in a pure state. The authors are obliged to Hynson, Westcott and Dunning,[10] Baltimore, Maryland, for supplying them with samples of pure phenol red, thymol blue and brom thymol blue.

Phenolphthalein.—A product obtained from J. T. Baker Company was recrystallized from methyl alcohol. According to the melting point and the result of the conductimetric titration it was quite pure.

Methyl **Red.—A** commercial product recrystallized from methyl alcohol took after drying the theoretical amount of sodium hydroxide.

A summary of the results obtained in the conductimetric titration of different samples of indicators is given in Table I.

TABLE I

CONDUCTIMETRIC TITRATION OF INDICATORS

Indicator	Origin	Alcohol concn. of soln. titrated, %	1st equiv. point Theoretical	1st equiv. point M. moles, found	2d equiv. point Theoretical	2d equiv. point M. moles, found
Brom thymol blue	Schering–Kahlbaum	20	0.160	0.153	0.321	0.330
Brom thymol blue	Same, purified	20	.160	.159	.321	.322
Brom thymol blue	National Aniline Co.	20	.160	.148	.321	.323
Phenol red	Schering–Kahlbaum	40	.283	.253	.567	.580
Phenol red	Same, purified	40	.283	.263	.567	.588
Phenol red	Same, recryst. from alc.	40	.283	.264	.567	.576
Phenol red	Hynson, Westcott and Dunning	40	.283	.260	.567	.571
Thymol blue	National Aniline Co.	40	.214	.179	.429	.412
Thymol blue	Hynson, Westcott and Dunning	80	.214	.197	.429	.424
Phenolphthalein	Purified	40			.629	.632
Methyl red	Purified	70	.372	.373		
Methyl red	National Aniline Co.	70	.372	.377		

The indicator solutions were prepared from the purified products. As a rule 100 mg. of a sulfonephthalein was dissolved in an equivalent amount of sodium hydroxide, in order to neutralize the sulfonic group. The solution was diluted with water to 100 cc. (solution of monovalent salt). To another 100 mg. of indicator double the amount of sodium hydroxide was added and the solution diluted to 100 cc. (solution of divalent salt). From these two standard solutions indicator mixtures of known PH were prepared

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[9] W. R. Omdorff and F. W. Sherwood, THIS JOURNAL, 45,486 (1923).

[10] According to our experience the indicators marketed by this company are of the purest obtainable in any country. It is peculiar that in the titration of pure phenol red the first break in conductivity appears before the complete neutralization of the sulfonic acid group.

in the way described above. With phenolphthalein as an indicator it is hard to prepare mixtures of known PH, as the first and second ionization constants are not known exactly and are of the same order of magnitude. Two 0.1% stock solutions of phenolphthalein in 50% alcohol were prepared: one with one equivalent sodium hydroxide (mono-), the other with two equivalents (di-). The right mixture was found empirically. From methyl red a 0.1% solution in 70% alcohol was prepared, and another in 50% alcohol with the same amount of indicator to which one equivalent of sodium hydroxide had been added.

Stability of Indicator Mixtures.—In agreement with the statement of other authors (especially Stern[6]) it was found that partly neutralized indicator solutions cannot be kept for a long time without changing their PH. This, of course, is especially the case with phenolphthalein, as the red quinoid is transformed into the carbonium salt. However, with partly neutralized brom thymol blue, thymol blue and phenol red solutions the authors had a similar experience. Usually the *PH* decreases after a few days' standing. This behavior, of course, has only to be considered in the determination of *PH* in pure water or solutions of neutral salts in pure water. If the solution to be tested has a distinct buffer action, it is immaterial whether the indicator solution used is exactly isohydric with the former.

For the measurement of PH in pure water or any other unbuffered solution, it is recommended that freshly prepared indicator mixtures be used and that these be made up fresh every two or three days. According to the authors' experience, there is no special advantage in keeping a complete series of solutions of an adjusted indicator, each differing 0.2 in *PH* from the other, as Fawcett and Acree recommend. The right mixture must be found in any case by empirical testing, and the series of adjusted solutions is not stable.

III. Technique of the Colorimetric PH Determination in Unbuffered Solutions.—In the *PH* measurement of pure water, neutral salt solutions in pure water and dilute solutions of sodium hydroxide, the liquid has to be protected from contamination by carbon dioxide (and other impurities of acid or basic nature) in the atmosphere. For the measurements described in this paper, the authors used a cell such as is shown in Fig. 1.

A sample of pure water is introduced into the Pyrex glass cell and made carbon dioxide free by passing through purified air which has been thoroughly washed by passing through soda lime, dilute sulfuric acid and several wash-bottles of pure water. After the water is carbon dioxide free (tests must be made after different times of passage of air, until the PH does not change further), a measured amount of the indicator mixture is added quickly from a pipet, by removing the glass stopper of the cell. During the addition of indicator the air is kept flowing through the cell.

Then after the solution is homogeneous, the taps A and B are closed and the color is compared with that of the same amount of indicator in a buffer solution kept in a cell of similar shape (glass stopcocks are not necessary here). After the reading the carbon dioxide-free air is again passed though the sample, and more indicator is added. After the color comparison a third portion of indicator is added. *If the correct indicator mixture is used, the same PH readings are found with different amounts of indicator.* If the *PH* found decreases with increasing amounts of indicator, the mixture is too acid, and if the *PH* decreases, the indicator mixture has too alkaline a reaction.

In the *PH* measurements of solutions of neutral salts in pure water, a measured volume of pure water was introduced into the cell and made carbon dioxide free, whereupon a weighed amount of salt was quickly added. The comparison was then made as described above. Several ***PH*** measurements have been made in extremely dilute sodium hydroxide solutions. It is one of the hardest problems to measure the *PH* of such solutions with any degree of accuracy. The hydrogen electrode is easily poisoned in such an unbuffered solution. The colorimetric method if properly applied gives excellent results, as will be shown in the experimental part.

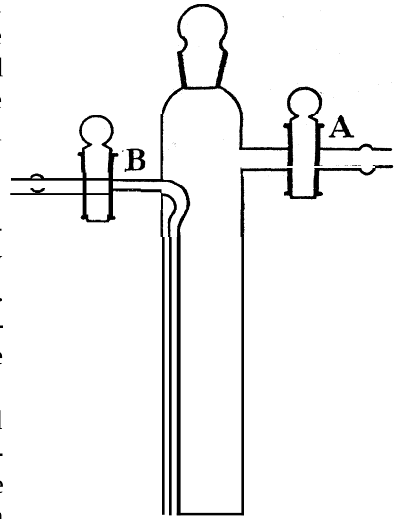

Fig. 1.

The water used was carefully prepared by distilling conductivity water over extremely dilute sulfuric acid to remove traces of volatile bases. The distillation was twice repeated without any addition and finally in a quartz apparatus with a quartz condenser. The first and last quarters of the distillate were discarded. The quartz receiver was protected by means of soda-lime tubes and wash-bottles containing very dilute sulfuric acid from atmospheric contamination. As a rule the water was used on the same day that the final distillation was made. It was siphoned from the quartz receiver into the pyrex cells. At least ten samples of water have been prepared, which after having been made carbon dioxide free showed a ***PH*** of **7.0** to **7.05**. **All** measurements have been made at a temperature of 25 ± 1.0°. Clark and Lubs buffer solutions were used for comparison, the *PH* of these being determined with the hydrogen electrode in a thermostat at 25°.

The *PH* value found with the isohydric indicator mixture must be corrected for the difference in ionic strength between the sample and the buffer solution. According to I. M. Kolthoff[6] a correction of **0.25** to **0.30** should be added to the *PH* found under the conditions mentioned in measurements in solutions with an ionic strength smaller than **0.0001** (water, and extremely dilute sodium hydroxide solutions) with brom thymol blue, phenol red, thymol blue and phenolphthalein as indicators. For methyl red the salt error is negligibly small,

IV. Experimental Results.—Fifteen cc. of water to which the indicated amounts of **0.1%** indicator mixtures were added was used. The water was practically carbon dioxide free when introduced into the cell; the *PH* was constant after passing through carbon dioxide-free air for thirty minutes. Some of the results obtained with mixtures of brom thymol blue and phenol red, respectively, are given in the following table.

TABLE II

COLORIMETRIC DETERMINATION OF *PH* IN 15 CC. OF PURE WATER AT 25°

Indicator	Ratio [HI⁻]/[I⁻]	*PH* for various volumes of indicator[a] 0.1 cc.	0.3 cc.	0.5 cc.
Brom thymol blue	96 : 4	6.62	6.50	6.20
Brom thymol blue	100 : 55	7.03	7.00	7.01
Brom thymol blue	4 : 96	7.93	8.05	8.25
Phenol red	99 : 1	6.70	6.60	6.50
Phenol red	100 : 10	7.03	7.05	7.07
Phenol red	1 : 99	8.55	8.85	9.00

[a] The observed *PH* has been increased by 0.25 to correct for the salt error.[5]

It appears that the mixtures of brom thymol blue, 100:55, and of phenol red, 100:10, are isohydric with the water. The corrected value of PH found in ten different experiments with different samples of water varied between **7.00** and **7.05.** The pure water is very sensitive to traces of carbon dioxide. After the water had been made carbon dioxide free the stopper of the cell was removed for one minute. The *PH* (corrected) dropped from **7.00** to **6.85.** Upon transferring this water–indicator mixture to another cell, the *PH* fell to **6.35.**

TABLE III

COLORIMETRIC DETERMINATION OF PH IN 15 CC. OF POTASSIUM CHLORIDE SOLUTION (AT 25°)

Indicator	Ratio [HI⁻]/[I⁻]	Concentration of 0.1 m.	0.25 m.	0.5 m.
Brom thymol blue[a]	100 : 55	6.77	6.77	6.77
Phenol red[a]	100 : 10	6.78	6.75	6.75
Hydrogen electrode[b]		6.70–6.77		

[a] No correction for salt error has been made. [b] Adapted for unbuffered solution, THIS JOURNAL, **53**, 821 (1931).

The following table gives values found in extremely dilute sodium hydroxide solutions. From the known hydroxyl ion concentration *PH* (theoretical) was calculated: *PH* = **14.00** − p_{OH} (25°). Measurements have been made with phenolphthalein and thymol blue, respectively, as indicators.

TABLE IV

COLORIMETRIC DETERMINATION OF *PH* IN (15 CC. OF) DILUTE SODIUM HYDROXIDE SOLUTION (AT 25°)

Indicator	Ratio $[HI^-]/[I^-]$	PA for various volumes of indicator[n] 0 1 cc.	0.3 *cc.*	0.5 cc	Theoretical
Phenolphthalein	99 : 1	9.30	9.30	9.30	9.22
Phenolphthalein	70 : 30	9.32	9.42	9.50	9.22
Phenolphthalein	60 : 40	9.40	9.50	9.60	9.22
Thymol blue	30 : 70	9.25	9.25	9.25	9.22
Thymol blue	50: 50	9 25	9.15	9.10	9.22
Phenolphthalein		9.30	9.28	..	9.22
Phenolphthalein		9.45	..	..	9.47
Phenolphthalein	...	9.73		..	9.82
Phenolphthalein		9.87	..	..	10.00
Phenolphthalein	...	10.05	..	..	10.12

[a] The observed *PH* has been increased by 0.25 to correct for the salt error.[5]

From these experiments it may be inferred that the PH of extremely dilute sodium hydroxide solutions can be determined with an accuracy of at least **0.1** if isohydric solutions of phenolphthalein or thymol blue are used as indicators and the proper correction for the salt error is added to the experimental figure. Recently J. W. McBain, O. E. Dubois and K. G. Hay, and J. W. McBain, M. E. Laing and O. E. Clark[11] have given data showing that phenol red, o-cresol red, phenolphthalein and thymol blue cannot be used for the colorimetric determination of PH in extremely dilute sodium hydroxide solutions, as the experimental figures differ by more than one to two units from the theoretical ones. From the above it is quite evident that this conclusion is unwarranted if precautions are taken against contaminations by carbon dioxide and if isohydric buffer solutions are used and the proper salt correction is applied.

Finally, it may be mentioned that the PH of pure zinc sulfate solutions has been measured with adjusted methyl red as indicator. At concentrations of zinc sulfate below **0.1** molar the colorimetric readings agreed within **0.01** in PH with the figures obtained with the hydrogen electrode. Details will be given in a paper on the hydrolysis of zinc sulfate.

Summary

1. Commercial indicators were purified by recrystallization and the purity tested by conductimetric titrations with sodium hydroxide.

2. A technique has been described for the colorimetric measurement of PH in pure water, of neutral salts in pure water and of extremely dilute sodium hydroxide solutions.

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[11] J. W. McBain, O. E. Dubois and K. G. Hay, *J.* Gen. Phys., 9, 461 (1926); J. W. McBain, M. E. Laing and O. E. Clark, *ibid.*, 12, 695 (1929).

3. In using isohydric indicator solutions and applying the proper salt corrections, the PH of pure water has been determined with brom thymol blue and phenol red at 25° with an accuracy of 0.05 in PH. With isohydric phenolphthalein or thymol blue solutions, the *PH* of extremely dilute sodium hydroxide solutions has been measured with an accuracy of 0.1 in PH.

MINNEAPOLIS, MINNESOTA

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

THE HYDROLYSIS OF ZINC SULFATE SOLUTIONS, SOLUBILITY PRODUCT OF HYDROUS ZINC OXIDE AND THE COMPOSITION OF THE LATTER PRECIPITATED FROM ZINC SULFATE SOLUTIONS

BY I. M. KOLTHOFF AND TOHRU KAMEDA[1]

RECEIVED JUNE 9, 1930 PUBLISHED MARCH 6, 1931

1. Hydrolysis of Zinc Sulfate.—For two reasons no reliable data on the hydrolysis of solutions of zinc sulfate are given in the literature; in the first place, no careful attention has been paid to the preparation of pure zinc sulfate, and in the second place the accurate measurement of the hydrogen-ion activity in zinc sulfate solutions is relatively difficult. The latter solutions have an extremely small buffer capacity, and on account of the hydrolytic adsorption by platinized platinum described in a former paper,[2] the ordinary type of platinized hydrogen electrode does not give reliable or reproducible results. The use of the quinhydrone electrode too is rather precarious in slightly buffered solutions. The authors have applied this electrode in all measurements described in this paper, but the readings were reproducible no better than to within 0.04 to 0.05 in PH, which was not considered sufficiently accurate for this type of work. Finally, the colorimetric method involves some complications on account of the salt influence upon the color of an indicator at constant activity of the hydrogen ions. In the present work the PH has been determined with a hydrogen electrode adapted to measurements in unbuffered solutions and described in a former paper.[3] The platinum wire was coated with a bright layer of platinum; after each set of measurements it was cleaned with aqua regia, ignited and replated. For details regarding manipulation the reader is referred to the former paper.[3]

The measurements were reproducible to within 0.01 to 0.02 of *PH*. In a former study[4] it had been found that the salt error of methyl red is negli-

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[1] From the experimental part of a thesis submitted by T. Kameda to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] I. M. Kolthoff and T. Kameda, THIS JOURNAL, 51, 2888 (1929).

[3] I. M. Kolthoff and T. Kameda, *ibid.*, 53, 821 (1931).

[4] I. M. Kolthoff, J. *Phys. Chem.*, 32, 1820 (1928).

gibly small in solutions with an ionic strength smaller than 0.5. For this reason the colorimetric method was applied with adjusted methyl red solutions[5] as indicator. At concentrations of zinc sulfate below 0.1 molar the electrometric and colorimetric methods gave exactly identical results.

Materials Used

Zinc Sulfate.—C. P. zinc sulfate was repeatedly recrystallized from conductivity water, until methyl red added to 0.5 g. of salt dissolved in 15 cc. of water indicated within 0.01 in PH a constant hydrogen-ion concentration. The products from the sixth, seventh and eighth recrystallization showed the same acidity and the salt after the seventh recrystallization was used in this work.

The recrystallization of the zinc sulfate has to be done very carefully; if the salt is boiled with water for some time a scum of basic sulfate is formed, and the crystals obtained in cooling the filtrate have too acid a reaction. In this work the zinc sulfate was added to conductivity water which was kept at about 70° in a larger bath. After the crystals had been dissolved by mechanical stirring, the solution was cooled in an ice-bath, repeatedly stirred and the salt collected by suction.

Water.—The water used as a solvent was obtained from conductivity water by distillation over very dilute sulfuric acid and finally in a quartz apparatus without any further addition. It was protected from atmospheric contamination.[3,5]

Methyl Red.—A product which was 99% pure was recrystallized from methyl alcohol. The conductimetric titrations with sodium hydroxide gave the calculated results. A solution of 100 mg. of indicator in 70% alcohol was prepared. A 0.1% solution of the sodium salt in 50% alcohol was obtained by adding the equivalent amount of sodium hydroxide. From these two stock solutions the adjusted mixtures were prepared.[5]

Buffer Solutions.—Biphthalate–sodium hydroxide buffers with an interval of 0.1 in PH were used. The PH values of these were checked with the hydrogen electrode at 25°. The colorimetric determinations were made at the same temperature.

Results

In Table I the results of the measurements are reported. The first column gives the concentration of zinc sulfate (moles per liter), the second the *P*H measured with the hydrogen electrode, the third the data found colorimetrically. The fourth column gives figures graphically interpolated from measurements made by M. Quintin[6] (using the quinhydrone elec-

TABLE I

HYDROLYSIS OF ZINC SULFATE AT 25°

Concn. of $ZnSO_4$, molar	PH acc. to K. and K.		Quintin	Denham and Marris
	H_2 electrode	Colorim. (m. red)		
0.01	6.00	6.00	5.52	5.09
.02	5.89	5.90	5.30	5.21
.05	5.76	5.77	5.03	5.3
.10	5.67	5.66	4.8	..
.25	5.26	5.48	..	..
.50	5.08	5.30	4.28	..

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[5] I. M. Kolthoff and T. Kameda, THIS JOURNAL, 53, 822 (1931).

[6] M. Quintin, *J. chim. phys.*, 24, 712 (1925).

trode), and the last column gives interpolated data of H. G. Denham and N. A. Marris[7] (also obtained with the quinhydrone electrode).

The figures obtained by the writers are quite different from those of Quintin.[6] Apparently he used a preparation containing a trace of free acid. The figures of Denham and Marris[7] are irregular; a study of their paper shows that the measurements are not well reproducible;[8] moreover, according to their report the *PH* increases with increasing zinc sulfate concentration, which seems highly improbable.

From the table it will be seen that the electrometric and colorimetric data obtained by the authors agree within 0.01 in *PH* up to a concentration of 0.1 molar. At higher concentrations the colorimetric reading gives a higher PH than the hydrogen electrode indicates. This may be caused by a salt error of the indicator at these high ionic strengths. However, it should be mentioned that at these high concentrations of zinc sulfate the measurements with the hydrogen electrode are not as well reproducible (to about 0.08 PH) as those in more dilute solutions. In order to test the magnitude of the salt error of methyl red at high ionic strengths, electrometric (hydrogen electrode) and colorimetric (methyl red) measurements have been made in 0.01 N acetate buffers in the presence of large amounts of sodium sulfate, magnesium chloride and magnesium sulfate.

TABLE II

SALT ERROR OF METHYL RED AT HIGH IONIC STRENGTH

Concn. of salt in 0.01 N acetate buffer, molar		PH, electr.	Pa, color.	Salt error of methyl red
Na_2SO_4	0.25	5.48	5.59	+0.11
$MgCl_2$	.25	5.38	5.50	+ .12
$MgSO_4$	.25	5.39	5.56	+ .17
$MgSO_4$	.5	5.30	5.52	+ .22

Magnesium sulfate is a salt of the same type as zinc sulfate, and it appears that if added to the acetate buffer the difference between the electrometric and colorimetric reading is of the same order as in pure zinc sulfate solution. On account of the uncertainty in the results obtained with the hydrogen electrode in the latter solutions, no correction has been applied at these higher ionic strengths. Depending upon the strength of zinc hydroxide as a mono-acid or diacid base, the hydrolysis of zinc sulfate can take place according to the reactions

$$Zn^{++} + H_2O \leftrightarrows ZnOH^+ + H^+ \qquad (1)$$

$$Zn^{++} + 2H_2O \leftrightarrows Zn(OH)_2 + 2H^+ \qquad (2)$$

As a matter of fact both reactions can occur simultaneously. From the *PH* values obtained in zinc sulfate solutions, it can be calculated according

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[7] H. G. Denham and N. A. Marris, *Trans. Faraday Soc.*, 24, 510 (1928).

[8] See Ref. 7. On p. 512 of their paper they mention that the $[H^+]$ at a dilution of 32 is 1.6×10^{-6}; in the table on p. 514 a value of 5.05×10^{-6} is given.

to which equation the hydrolysis takes place. If it occurs according to (1)

$$\frac{[a\text{ZnOH}^+]\,[a\text{H}^+]}{[a\text{Zn}^{++}]} = K_{1\,\text{hydr.}} \tag{3}$$

K should be constant. In the other case the equation

$$\frac{[a\text{Zn(OH)}_2]\,[a\text{H}^+]^2}{[a\text{Zn}^{++}]} = K_{2\,\text{hydr}} \tag{4}$$

should hold. From the experimental figures it appears that the hydrolysis takes place according to (1) and is quantitatively expressed by **(3).** In the calculation of $K_{\text{hydr.}}$ (Eq. *3)* it is assumed that the activity of the ZnOH$^+$ ions is equal to the hydrogen-ion activity $[a\text{H}^+]$. This will be approximately true in the more dilute solutions, at higher ionic strengths the difference between the activity coefficients of both ions probably will be no longer negligibly small. However, we have no means of determining the activity of ZnOH$^+$ ions separately, and therefore this assumption must be made. The activity of the zinc ions ($[a\text{Zn}^{++}]$) in zinc sulfate solutions has been taken from an experimental study of U. B. Bray,[9] assuming that the activities of the zinc and sulfate ions are equal at the same ionic strength. The values of the hydrolysis constant are given in the following table.

TABLE III

HYDROLYSIS CONSTANT (EQ. 3) IN ZINC SULFATE SOLUTIONS AT 25°

Concn. of zinc sulfate. *molar*	$[a\text{H}^+] \times 10^6$	$[a\text{Zn}^+]$	$K_{\text{hydr.}} \times 10^{10}$
0.01	1.00	4.2×10^{-3}	2.4
.02	1.26	6.4×10^{-3}	2.60
.05	1.70	1.1×10^{-2}	2.76
.1	2.14	1.61×10^{-2}	2.84
		Average	2.65

As the PH values in the more concentrated zinc sulfate solutions are rather uncertain, the figures obtained in these solutions have not been used for the calculation of the hydrolysis constant. From the figures given in the table, it appears that $K_{\text{hydr.}}$ is constant within 10% at zinc sulfate concentrations between 0.01 and 0.1 molar. Therefore the hydrolysis according to Equation 2 is negligibly small, and it may be inferred that zinc hydroxide with regard to its first step of ionization behaves like a strong base. Considering the similarity between magnesium and zinc hydroxide, this result could be expected. The second ionization constant of zinc hydroxide

$$\text{ZnOH}^+ \rightleftarrows \text{Zn}^{++} + \text{OH}^-$$

$$\frac{[a\text{Zn}^{++}]\,[a\text{OH}^-]}{[a\text{ZnOH}^+]} = \frac{K_w}{K_{\text{hydr.}}}$$

has been calculated from the hydrolysis constant and the ionic product of water. At 25° $K_w = 1.00 \times 10^{-14}$, and for $K_{\text{hydr.}}$ an average value of

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[9] U. B. **Bray,** THIS JOURNAL, 49, **2372 (1927).**

2.65×10^{-10} has been found. Therefore the second ionization constant of zinc hydroxide at 25° is equal to **3.8** (± 0.3) $\times 10^{-5}$, which is about twice as large as the basic constant of ammonia.

It may be mentioned that all values of PH have been calculated by using the standard values originally given by S. P. L. Sörensen,[10] and advocated by W. M. Clark.[11] The Sorensen values do not exactly correspond to the activity exponents of the hydrogen ions. Accepting the relation

$$Pa_{H} = P_{H} + 0.04$$

(Pa_{H} is the negative logarithm of the activity of the hydrogen ions and PH is the hydrogen-ion exponent according to Sorensen), it is found that $K_{\text{hydr.}} = 2.2 \times 10^{-10}$ and K_2 of zinc hydroxide is 4.4 (± 0.4) $\times 10^{-5}$. Finally it may be mentioned here that the authors have found no indications whatsoever that the PH of zinc sulfate solutions changes on standing.[12] If kept in pyrex bottles (or Jena glass) the *PH* is unaltered after a few months' standing.

2. Solubility Product of Hydrous Zinc Oxide and the Composition of the Latter Obtained by Precipitation from Zinc Sulfate **Solution.**—Solutions of pure zinc sulfate of various strengths were titrated at 25+ 0.1° with sodium hydroxide, the latter usually having a concentration about ten times larger than the zinc solution. During the titration the PH was measured by means of a hydrogen electrode. The titration cell as shown in Fig. 1 is very suitable for this purpose. Again a platinum wire coated with a bright layer of platinum was used. With an electrode coated with platinum black the results were not quite reproducible, and it is difficult to find the values with an accuracy of 0.1 in PH. With the wire coated with a bright layer of platinum the readings were reproducible to within 0.02. Replating is necessary after each set of measurements.

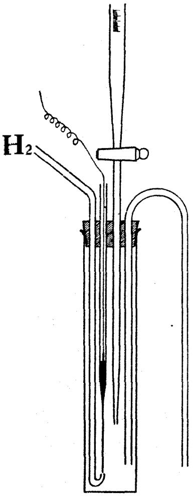

Fig. 1

After the addition of 1 to 2% of the equivalent amount of sodium hydroxide, the hydrous zinc oxide begins to precipitate; from this point on the PH increases very slightly on further addition of sodium hydroxide. In the following table the *PH* values at which the precipitation of the hydrous zinc oxide starts are indicated. As the zinc concentration was known at this point, the solubility product could be calculated. The activity of the zinc ions again was found from the data

$$[a\text{Zn}^{++}]\,[a\text{OH}^-]^2 = S_{\text{Zn(OH)}_2x\text{H}_2\text{O}}$$

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[10] *S. P. L.* Sörensen, *Compt.-rend. trav. lab. Carlsberg,* 8, *23* (1909).

[11] *W. M. Clark, "The Determination of Hydrogen Ions,"* 3d *ed., The Williams and Wilkins Co., Baltimore, Maryland,* 1928.

[12] *See H. G.* Denham, *J. Chem. Soc.,* **93, 41 (1908).**

given by U. B. Bray? At 25°, $P_{OH} = 14.00 - P_H$. If the solubility of the hydrous zinc oxide at 25° is s, and the saturated solution is completely dissociated into the ions, which practically is the case as may be inferred from the magnitude of the second ionization of zinc hydroxide, then $s = \sqrt[3]{S/4}$.

The values of s expressed in moles per liter are given in the table. It appears that the apparent solubility product is not quite constant, but decreases with increasing zinc concentration in the solution. The product $[c\mathrm{Zn}^{++}]\ [a\mathrm{OH}^-]^2$, in which $[c\mathrm{Zn}^{++}]$ indicates the total zinc-ion concentration, yields a value which is a much better constant than $[a\mathrm{Zn}^{++}]\ [a\mathrm{OH}^-]^2$. The corresponding values are included in the table. The first column gives the concentration of the zinc sulfate solution titrated, the second the P_H values computed on the basis of Sörensen's standard values, the third column the solubility product $[a\mathrm{Zn}^{++}]\ [a\mathrm{OH}^-]^2$, the fourth one the corresponding solubility s, and the last column the product $[c\mathrm{Zn}^{++}]\ [a\mathrm{H}^+]$.[2]

TABLE IV

SOLUBILITY PRODUCT OF HYDROUS ZINC OXIDE

Concn. of zinc sulfate, molar	P_H at precipitation of hydrous oxide	$S = [a\mathrm{Zn}^{++}][a\mathrm{OH}^-]^2 \times 10^{18}$	$s \times 10^6$	$[c\mathrm{Zn}^{++}][a\mathrm{OH}^-]^2 \times 10^{18}$
0.01	6.49	4	1.0	9.5
.05	6.17	2.5	0.85	10.9
.25	5.80	1.0	.64	9.9

H. T. S. Britton,[13] who studied the precipitation of hydrous zinc oxide, found that in 0.025 molar zinc sulfate solution the precipitation started at a P_H of 5.2 (at 18°). This value is more than one unit lower than that found by the authors. Accordingly Britton calculated a solubility product of the order of 10^{-21}, which is about 1000 times smaller than the figure in the above table. Probably some error must have been introduced in Britton's measurements of P_H. From the curve in his paper (p. 2125) it can be calculated that the P_H in 0.025 molar solution of pure (?)zinc sulfate is 3.8, whereas this figure according to our measurements is 5.87!

The figures found by the authors are of the same order of magnitude as those reported by H. G. Dietrich and J. Johnston[14] and Miss de Wÿs.[15] The former calculate a solubility of 2×10^{-6} molar, the latter of 2.7×10^{-6}. The value found by the authors is about 1×10^{-6}, whereas other data reported in the literature are much higher.[16]

As will be discussed below, the hydrous zinc oxide precipitated by sodium hydroxide contains some sulfate in a ratio of about $3\mathrm{ZnO}:1\mathrm{ZnSO_4}$. Die-

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[13] H. T. S. Britton, *J. Chem. Soc.*, 125, 2124 (1927).

[14] H. G. Dietrich and J. Johnston, THIS JOURNAL, 49, 1419 (1927).

[15] De Wys, *Rec. trav. chim.*, 44, 663 (1925).

[16] Bodlander, *Z. physik. Chem.*, 27, 66 (1898), gives 1.25×10^{-5} molar; Hen, *Z. anorg. Chem.*, *23*, *222* (1900), 1.3×10^{-5}; Dupré and Biala, *Z. angew. Chem.*, *16*, *54* (1903), 5.2×10^{-5}; Remy and Kuhlmann, *Z. anal. Chem.*, *65*, 161 (1924), 3.7×10^{-5}.

trich and Johnston,[11] as well as de Wÿs,[15] used crystalline zinc hydroxide in their work. In order to obtain a better comparison with their data, measurements of PH have been made in zinc sulfate solution saturated with different kinds of zinc hydroxide and zinc oxide. In addition the neutralization curve of zinc chloride (instead of zinc sulfate) with sodium hydroxide has been determined at 25°. The hydrous zinc oxide formed in the latter case contains only a small fraction of chloride. The zinc chloride solution was obtained by adding an equivalent amount of barium chloride solution to zinc sulfate.

Crystalline zinc hydroxide (a) was obtained according to the directions of H. G. Dietrich and J. Johnston by crystallization from an ammoniacal solution. The crystals obtained were kept in a desiccater over deliquescent sodium bromide for two years. The water content determined by ignition in an electric furnace at 800° was 18.18% (calcd., 18.11%).

Another crystalline product (b) was obtained by precipitation of zinc sulfate with an excess of ammonia. The product was carefully washed in a mortar with water, during which time it changed into a definite crystalline compound—zinc oxide. Products a and b were heated in an electric furnace for about three hours at 800°.

0.05 Molar zinc sulfate was saturated at 25° in the hydrogen electrode cell adapted for measurements of unbuffered solutions with the different products of zinc hydroxide and zinc oxide. The data are reported in **Table** V. The figures obtained in the precipitation of zinc sulfate and zinc chloride with sodium hydroxide are also included.

TABLE V

PH OF 0.05 MOLAR ZINC SULFATE SATURATED WITH DIFFERENT KINDS OF ZINC HYDROXIDE OR ZINC OXIDE AT 25°

Zinc hydroxide or oxide	PH	Remarks
Cryst. $Zn(OH)_2$ (a)	6.13	All solutions have a colloidal appearance on shaking with the different preparations.
Cryst. $Zn(OH)_2$ (b)	6.16	
ZnO by ignition of (a)	6.22	
ZnO by ignition of (b)	6.12	
Freshly pptd. by NaOH	6.17	
Freshly pptd. by NaOH in 0.05 molar $ZnCl_2$	6.19	

In all cases the PH measured is the same within 0.05 as in the zinc sulfate solution to which a trace of sodium hydroxide has been added, whereas one would expect individual differences between the different solutions as the solids present in excess have different compositions and crystal structures. However, it seems doubtful whether these different modifications are stable in a zinc sulfate solution; on shaking, all solutions assume a colloidal appearance as in zinc sulfate with a small amount of sodium hydroxide.

In Fig. 2 the change in PH during the titration of 0.01 molar and 0.05 molar zinc sulfate with 0.2 *N* sodium hydroxide and of 0.25 molar zinc sulfate with 1 *N* sodium hydroxide have been given. The abscissa gives the percentage of the equivalent amount of sodium hydroxide added.

In each case the *P*H values have been determined in the hydrogen electrode titration cell usually after addition of 0, 2, 4, 6, 8, 10, 25, 40, 60, 70, 75, 78, 80, 82, 85, 90, 95 and 100% of the equivalent amount of base. Moreover, the curve in the titration of 0.05 molar zinc chloride under similar conditions has been given. **A** jump in potential occurs at a PH approximately between 7 and 10, long before an equivalent amount of sodium hydroxide has been added. This indicates that a basic zinc sulfate or hydrous oxide containing adsorbed sulfuric acid is formed. The location of the jump is almost independent of the concentration of the zinc solutions titrated. Figures are given in Table VI.

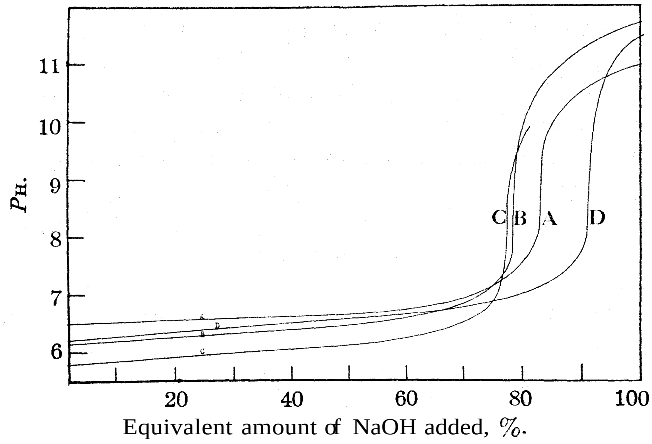

Fig. 2.—Potentiometric titration curves of zinc sulfate with sodium hydroxide. A, 25 ml. of 0.01 M $ZnSO_4$ titrated with 0.1981 *N* NaOH; B, 25 ml. of 0.05 M $ZnSO_4$ titrated with 1.0046 *N* NaOH; C, 25 ml. of 0.25 M $ZnSO_4$ titrated with 1.0046 M NaOH; D, 25 ml. of 0.05 M $ZnCl_2$ titrated with 0.1988 M NaOH.

TABLE VI

END-POINTS IN ZINC SULFATE TITRATION DERIVED FROM POTENTIOMETRIC TITRATION AT 25°

Solution, molar		Jump in potential after addition of NaOH equivalents to
$ZnSO_4$	0.01	83%
$ZnSO_4$	.05	79%
$ZnSO_4$	.25	78%
$ZnCl_2$	.05	92%

The precipitate formed in the titration of zinc chloride is much less basic than that from zinc sulfate. H. T. S. Britton[13] found the precipitation of 0.025 molar zinc sulfate complete after addition of 77.5% of the equivalent amount of sodium hydroxide, which is in good agreement with the data reported.

It seemed interesting to investigate how the composition of the hydrous oxide formed changes during the precipitation. In the titration of aluminum sulfate with sodium hydroxide Miller[17] has found that the hydrous oxide precipitated contains more acid, the less base has been added. As will be shown below, the precipitate formed on the addition of sodium hydroxide to zinc sulfate has a fairly constant composition until quite near the end-point.

In addition it was of interest to see how the P_H of the solution and the composition of the precipitate change on aging. In one set of experiments mixtures of zinc sulfate and sodium hydroxide were shaken for ten days at 25° and thereafter analyzed. In another set mixtures were kept for three hundred days at room temperature and then analyzed. Finally the temperature effect has been studied by heating mixtures of zinc sulfate and sodium hydroxide for ten days at 80°; they were analyzed after cooling.

The experiments were made in the following way. Known amounts of zinc sulfate dissolved in water were mixed with a definite volume of standardized sodium hydroxide. The mixture was immediately diluted with water in a volumetric flask so that the initial concentration of zinc sulfate in all cases corresponded to 0.05 molar. Immediately or after the indicated time of standing the P_H was determined with the hydrogen electrode adapted for measurements of unbuffered solutions. The filtrate was used for the further analysis. In part of the filtrate the P_H was determined colorimetrically with adjusted brom thymol blue as an indicator. The data obtained were not exactly the same as those found potentiometrically. As the salt error of the indicator under the conditions of these experiments is not exactly known, the data found colorimetrically have been omitted in the tables. In another part of the filtrate the zinc concentration was determined by precipitation with o-hydroxyquinoline. The precipitate was weighed or, if the zinc concentration was very small, titrated bromometrically. Both procedures give very accurate results. From the original zinc sulfate content, the amount of base added and the zinc concentration found in the precipitate, the composition of the hydrous oxide could be calculated. However, in order to check the analyses in all cases, the sulfate content in the filtrate was determined by a conductimetric titration with barium chloride in a thermostat at 25°. Details of this investigation will be described elsewhere. It may be stated here that the results calculated from the zinc analysis checked to within 1% with those obtained from the sulfate titrations.

Table VII gives the change of P_H of zinc sulfate solutions to which small amounts of sodium hydroxide had been added. The electrometric measure-

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[17] Miller, *U. S. Publ. Health Repts.*, **38**, 1995 (1923).

ments were made at 25° immediately after addition of base, after fifteen days' shaking at room temperature and after sixteen days' heating at 80°.

TABLE VII

EFFECT OF AGING UPON P_H OF ZINC SULFATE WITH SMALL AMOUNTS OF SODIUM HYDROXIDE

Concn. of zinc sulfate, molar	Added sodium hydroxide in equivalents	P_H immediately after mixing	P_H after 16 days at 25°	P_H after 16 days at 80°
0.01	5%	6.49	6 42	6.29
.05	5%	6.17	6 09	5.94
.25	5%	5.80	5.80	5.72

In Table VIII a summary of all the analytical results has been given. In all cases the original concentration of zinc sulfate was equal to 0.05 molar. The first column gives the equivalent amount of sodium hydroxide added expressed in percentage, the second column the composition of the precipitate by the ratio $ZnO:ZnSO_4$ as derived from the analysis after immediate filtration. The third gives the same ratio after ten days' shaking at room temperature and the fourth the same after standing for ten days at 80°.

TABLE VIII

COMPOSITION OF HYDROUS ZINC OXIDE BY PRECIPITATION FROM 0.05 MOLAR ZINC SULFATE

Equivalent amount of sodium hydroxide added	Ratio $ZnO:ZnSO_4$		
	Immediately after precipitation	After 10 days at 25°	After 10 days at 80°
25%	3.2:1	3.3:1	5.9:1
50%	3.1.1	3.5:1	5.0:1
75%	3.2:1	3.7 1	4.6:1

Finally, Table IX shows the effect of aging for three hundred days at room temperature upon the composition of the precipitate.

TABLE IX

COMPOSITION OF HYDROUS ZINC OXIDE AFTER 300 DAYS AT ROOM TEMPERATURE

Equivalent amount of sodium hydroxide added to 0.05 molar zinc sulfate	10%	20%	50%	80%	90%
Ratio $ZnO:ZnSO_4$ in precipitate	3.5:1	3.6:1	3.4:1	4.2:1	8.8:1

From the last three tables it may be inferred that the composition of hydrous zinc oxide precipitated from zinc sulfate solution by sodium hydroxide is fairly constant from the beginning to the end of the precipitation, corresponding to the separation of a basic salt $3ZnO \cdot ZnSO_4 \cdot xH_2O$. The jumps in potential in the potentiometric titration discussed before also indicate approximately a similar composition. Pickering[18] concluded that after complete precipitation of all the zinc the precipitate had the composition $4ZnO \cdot ZnSO_4$. However, it seems that just at the equivalence point, where no excess of zinc sulfate is present, the precipitate is no longer

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[18] Pickering, *J. Chem. Soc.*, 91, 1981 (1907).

stable, as may be seen from the last two figures in the last table. According to Zubkowskaja[19] only the basic salt $3ZnO\cdot ZnSO_4\cdot xH_2O$ is a definite compound. The latter is slowly decomposed by water, as shown by experiments of W. Feitknecht.[20]

From experiments of the latter, one would conclude that the basic salt is only stable in 0.00075 molar zinc sulfate or more concentrated solutions. Therefore, the composition derived from experiments where the precipitation is just complete, has no exact significance. The basic compound is fairly stable at room temperature; even after standing for three hundred days with the supernatant liquid the basicity of the precipitate increases only slightly ($3.5ZnO:ZnSO_4$) whereas the **PH** of the solution practically does not change. However, at higher temperatures the precipitate loses acid and becomes definitely more basic. Accordingly the **PH** of the supernatant liquid decreases, as may be seen from the tables, in which the influence of heating for ten days at SO° has been shown. Though the composition of the precipitate formed at room temperature corresponds to $3ZnO\cdot ZnSO_4\cdot xH_2O$, it is not possible to conclude with certainty from the above experiments whether the latter is a definite compound. The fact that the ratio of $ZnO:ZnSO_4$ is constant during the entire precipitation is an indication in this direction.

Summary

1. An exact study has been made of the hydrolysis of solutions of pure zinc sulfate at 25°. It could be concluded that zinc hydroxide as a monoacid base is very strong; its second ionization constant at 25° is equal to $4.4\ (\pm 0.4) \times 10^{-5}$.

2. The solubility of hydrous zinc oxide precipitated from zinc sulfate is at 25° about 1×10^{-6} molar. This figure is smaller than most data reported in the literature.

3. The PH of a zinc sulfate solution saturated with zinc hydroxide is practically independent of the kind of zinc hydroxide or zinc oxide present as solid.

4. The hydrous oxide formed on the addition of sodium hydroxide to zinc sulfate solutions at 25° has a fairly constant composition during the entire precipitation, corresponding to the formation of a basic salt $3ZnO\cdot ZnSO_4$. The effect of aging at room temperature is small. Heating the precipitate with the supernatant liquid for ten days at 80° changes the composition of the hydrous oxide. It becomes more basic, and the PH of the supernatant solution decreases.

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[19] Zubkowskaja, *Chem. Zentr.*, I, 797 (1908).

[20] W. Feitknecht, *Helv. Chim. Acta*, 13, 22 (1930).

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE CONSTANTS OF THE BEATTIE–BRIDGEMAN EQUATION OF STATE WITH BARTLETT'S P–V–T DATA ON HYDROGEN

BY W. EDWARDS DEMING AND LOLA E. SHUPE

RECEIVED JULY 14, 1930 PUBLISHED MARCH 6, 1931

In two previous papers, Bartlett[1] and his co-workers have published compressibility data for hydrogen, nitrogen and their 3:1 mixture to 1000 atmospheres pressure and from −70 to 400°. These included their own measurements and those from other sources. It is desirable to have a formula that will represent this compressibility data over as wide a range as possible in order that thermodynamic properties may be computed analytically. Accordingly the writers have attempted to find values for the constants in the Beattie–Bridgeman[2] equation of state for these data. The constants for nitrogen have already been published.[3] We here present the values of the constants for hydrogen; and in a later article we hope to present those for the 3:1 hydrogen–nitrogen mixture with a discussion of the scheme for combining the constants of the constituents to derive an equation for a mixture.

The method of determining the constants is a modification of that originally given by Beattie and Bridgeman and it was explained in detail in our paper on nitrogen. In the present work we use specific volumes in cc. per mole instead of cc. per gram; and we decided to use Birge's value[4] 22414.1 cc. for the volume of a mole of an ideal gas at S. T. P., and his value 273.18°K. for the ice point. The "International Critical Tables" (Vol. III, p. 3) give 0.99939 for the ratio of P V at 0° and 0 pressure to P V at 0° and 1 atm. pressure for hydrogen, so we use $22414.1/0.99939 = 22427.8$ cc. as the volume of a mole of hydrogen at S. T. P. This is the factor that converts Bartlett's volumes into cc. per mole. For R we use $22414.1/273.18 = 82.0489$ cc. atm. per mole per degree. In the previous work on nitrogen we used 273.13°K. for the ice point, but we think it is better to adopt Birge's values now. This change is too small to affect the constants in the equation of state because their values are fixed by the positions of certain lines or curves (Fig. 1), and in such work the locations of the curves are often a matter not easy to decide. Further, the ice-point enters mainly through the product RT, that is, through the volume of a mole of an ideal gas at 0° and 0 pressure, for which Birge's value is very

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[1] Bartlett, Cupples and Tremearne, THIS JOURNAL, 50, 1275 (1928); Bartlett, Hetherington, Kvalnes and Tremearne, *ibid.*, 52, 1364 (1930).

[2] Beattie and Bridgeman, *Proc. Am. Acad. Arts Sci.*, 63, 229 (1928); THIS JOURNAL, 49, 1665 (1927); and later papers.

[3] Deming and Miss Shupe, *ibid.*, 52, 1382 (1930).

[4] Birge, *Phys. Rev. Supplement*, 1, 1 (1929).

nearly the same as had commonly been accepted prior to his compilation of physical constants, so the use of 273.18° does not have any discernible effect on the values to be determined for the parameters.

Bartlett and co-workers compiled and published compressibility data from all available sources along with their own. For the determination of the parameters in the equation of state we decided to smooth and average all of these data, and at the same time to interpolate to even temperatures.[5] Our method for smoothing and averaging the observations of the different observers listed by Bartlett was to plot $D \equiv mT - PV + I$ against T. m and I are constants for each isobar; I is the intercept and m the slope of a line chosen to approximate PV plotted against T. There is a PV and hence a D for each observation in Bartlett's tables. Smooth isobars were drawn to the graphs of D *vs.* T. Bartlett's points were given the most weight because his observations extend over the greatest range. Values of D were read off these curves at even temperatures; and from them $PV = mT + I - D$ was computed at each temperature and pressure, using the same values of m and I for each isobar that were used in computing the D. These compressibility factors, which are shown in Table I, should be the most reliable yet published for hydrogen. Values at 400° are not shown, because, although Bartlett made determinations at 100, 200, 300 and 400 atmospheres at this temperature, he does not consider them to be reliable.

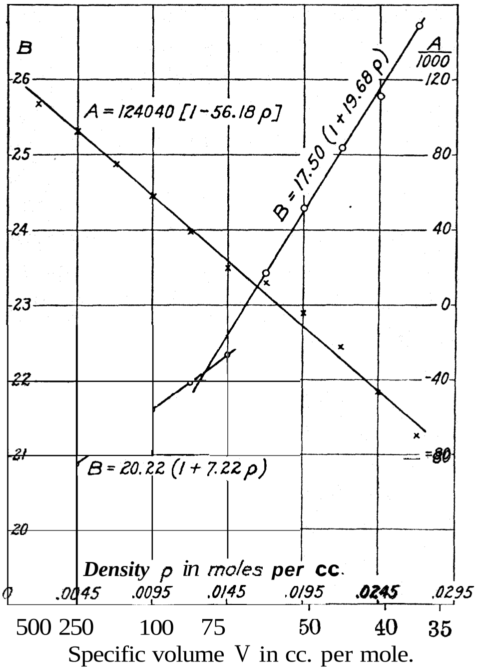

Fig. 1.—Hydrogen, The *A* and B plots.

For determining the constants in an equation of state it is better to have the pressures listed at even temperatures and densities than to have volumes listed at even temperatures and pressures. This change can be

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[5] In the first reference to Barlett and co-workers, some of the temperatures lacked a few tenths of being integral. Further, after the second reference had gone to the publisher, Dr. Kvalnes advised us that a recalibration of their thermocouple showed the temperatures published as –70, –50, –25° should have been –69.90, –49.93, –24.99°. In our Table I the compressibility factors are computed for integral temperatures.

TABLE I

AVERAGED AND SMOOTHED COMPRESSIBILITY FACTORS, PV, FOR HYDROGEN. $PV = 1$ AT 1 ATMOSPHERE AND 0°

T, °K.	203 18	223.18	248.18	273.18	293 18	323 18	373 18	473 18	573 18
T, °C.	−70	−50	−25	0	20	50	100	200	300
Pressure, atm.				Compressibility factors					
1	0.7437	0.8170	0.9085	1.0000	1.0732	1.1830	1.3661	1.7321	2.0981
25	.7562	.8295	.9218	1.0145	1.889	....	....	....	....
50	.7699	.8448	.9380	1.0311	1.1054	1.2166	1.4016	1.7692	....
75	.7848	.8604	.9543	1.0476	1.1221	....	....	....	....
100	.7993	.8755	.9701	1.0642	1.1391	1.2510	1.4366	1.8036	2.1662
125	.8139	.8930	.9906	1.0864	1.1610	....	....	....	....
150	.8310	.9081	1.0034	1.0979	1.1726	....	....	....	....
200	.8616	.9394	1.0358	1.1317	1.2082	1.3226	1.5121	1.8856	2.2545
300	.9319	1.0115	1.1095	1.2056	1.2821	1.3959	1.5844	1.9581	2.3274
400	1.0069	1.0848	1.1814	1.2772	1.3535	1.4676	1.6568	2.0313	2.4011
500	1.0796	1.1572	1.2540	1.3507	1.4280	....	....	....	....
600	1.1516	1.2330	1.3300	1.4257	1.5017	1.6152	1.8033	2.1764	2.5438
800	1.2989	1.3775	1.4732	1.5692	1.6451	1.7583	1.9462	2.3196	2.6803
1000	1.4439	1.5218	1.6172	1.7123	1.7878	1.9008	2.0877	2.4586	2.8158

effected by the following **method.**[6] $A \equiv (PV - RT)V/RT$ is plotted against $\rho = 1/V$ for each temperature and smooth isotherms are drawn. Then A is read off at even densities from each isotherm, and $P = RT(\rho - \rho^2 A)$ is computed for each temperature and volume. In this process the data are further smoothed. Pressures thus derived are listed in Table II at even temperatures and densities. The family of ρ, A isotherms were so regular that extrapolations beyond the highest observed densities seemed justified and, since they are to be desired, were made. We write

$$P + \Gamma = \psi T - \phi \qquad (1)$$

Beattie and Bridgeman put

$$\left.\begin{array}{lll} \Gamma T^2 = \psi c/V & \psi = R(V + B)V^{-2} & \phi = AV^{-2} \\ B = B_0(1 - b/V) & & A = A_0(1 - a/V) \end{array}\right\} \qquad (2)$$

with A,, V_0 a, b, c constants, mentioning the possibility of extending the expressions for A and B to include higher powers of $1/V$. The method that we used for finding the constants was described in the paper on nitrogen.

For the four highest densities, the best values of c are **10.4,** 19.7, 18.9, **23.9** × 10^6. They evidently increase as the density decreases. We adopted $c = 20 \times 10^6$ as the best average value. We then determined what values of ψ and ϕ with $c = 20 \times 10^6$ render the mean square per cent. deviations of the calculated pressures a minimum for each isochore. The values thus found were used to compute $A = \phi V^2$ and $B = (\psi V^2 - RV)/R$ for each density. A and B were then plotted against ρ.

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[6] Andrews, *Phil. Trans. Roy. Soc.*, 166, 421 (1876); O. C. Bridgeman, THIS JOURNAL, 49, 1130 (1927).

In the A plot, for the representation of compressibility data, a straight line suffices; yet there is an indication of a break at about 0.015 mole per cc. On the B plot two straight lines seem *to* be the only solution. For the representation of data the lines shown in the figure are probably the best that can be drawn; yet for a theoretical discussion the break in the B points comes at a somewhat higher density than is indicated by the intersection of the two lines. It looks as if the location of the breaks on both plots are close to the critical density, which is 0.0154 mole per cc. With the lines as drawn in the figure there will be one set of values for $A,$ and a throughout the entire range of densities, but there will be two sets for B_0 and b, one set for densities below the critical density and another set for densities above it.

Since the points on both the A and B plots from the lowest density to the critical density lie almost perfectly on the lines shown, we can say that the Beattie–Bridgeman equation of state holds almost perfectly up to the critical density.

From the figure it will be seen that $\phi = A\rho^2$ becomes negative at the highest densities. It is customary to regard ϕ as a cohesive pressure. It may be identified with the a/V^2 in van der Waals' equation as it is usually written. It evidently arises from the forces between molecules and will be positive when such forces are attractive. Its sign should change, however, if the forces between molecules become repulsive instead of attractive. The generally accepted working hypothesis for the forces between two molecules predicts that as two molecules come closer and closer together, the force changes from attraction to repulsion. Now at the high densities reached in the experimental work done by Bartlett and co-workers, the molecules of hydrogen may be in such concentration that this change in force is actually brought about, which causes ϕ to decrease and eventually to change sign. This same phenomenon and one allied to it have been noticed with nitrogen and with the **3:1** mixture.

The values for the constants that are determined by the plots in Fig. 1 are

$$\left.\begin{array}{llll} \text{Below the critical density:} & A, = 124040 & B_0 = 20.22 \\ \qquad a = 56.18 & b = -7.22 & c = 20 \times 10^6 \\ \textbf{Above} \text{ the critical density:} & A, = 124040 & B_0 = 17.50 \\ \qquad a = 56.18 & b = -19.68 & c = 20 \times 10^6 \end{array}\right\} \quad (3)$$

Beattie and Bridgeman, in their first paper, gave

$$\begin{array}{llll} A_0 = 197500 & B_0 = 20.96 & a = -5.06 & b = -43.59 \\ c = 50.4 \times 10^4 \end{array} \quad (4)$$

for the values of the constants determined from data published by the Leiden Laboratory, the Reichsanstalt, and Witkowski, in which the highest pressure at each temperature down to −150° was about 100 atm., and in which the temperature range was from −212.74 to 200°. Pressures calculated with the constants of Equations 4 do not agree with the pressures of Table II as well as do the constants in Equations 3, as is shown by the following tabulation of root mean square deviations at the five lowest densities. The second column is anticipated from Table II.

Density	R. M. S. per cent. deviations using Equations 3	Equations 4
0.0020	0.040	0.129
.0045	.048	.398
.0070	.058	1.30
.0095	.100	2.63
.0120	.166	4.25

At higher densities the disparity becomes still more pronounced. On the other hand, the constants of Equations 3 give larger deviations than Equations 4 at the extremely low temperatures at which observations have been made at the Leiden Laboratory. Over the range of density and temperature of Table II the constants in Equations 3 seem to be the best that can be obtained.

Table II lists the smoothed pressures at even temperatures and densities and the comparison with the calculated pressures.

Consideration of the deviations in Table II shows that the constants given in Equations 3 reproduce pressures for hydrogen very well up to 0.0245 mole per cc. inclusive, and with a root mean square error of 1.4% for the five lowest temperatures at 0.0270 mole per cc.

These calculations were made with the two sets of values for B_0 and b, corresponding to the two lines for the B points in the figure. No single set of constants (*i. e.*, no single straight line) will give anywhere near as good agreements between observed and calculated pressures. A parabola cannot be fitted satisfactorily to the B points. The only solution seems to be the two straight lines.

PV values at 400° were calculated and compared with those observed and published by Bartlett, and we find deviations of —1.04, —0.47, —0.62, —0.37% at 100, 200, 300, 400 atm., respectively. This probably confirms Bartlett's suspicion that his observations at 400° may not be reliable, because these are larger deviations than one would expect from an extrapolation of 100" above the interval —70 to 300° at comparatively low pressures. The negative sign of the deviations probably indicates that his measured values of V were too small—perhaps due to gas escaping from or diffusing through the pipet at this high temperature, as was suspected by Bartlett and co-workers.'

We have had the willing coöperation of the staff of the Fixed Nitrogen Research Laboratory and of the authors of the equation of state throughout the course of this work.

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[7] Bartlett, Cupples and Tremearne, THIS JOURNAL, 50, 1275 (1928).

Table II

OBSERVED PRESSURES AT EVEN DENSITIES AND TEMPERATURES AS SMOOTHED FROM THE COMPILATIONS OF BARTLETT AND CO-WORKERS.

HYDROGEN

Comparison with pressures calculated from the Beattie–Bridgeman equation of state, using the constants of Equation 3. Volumes are in cc. per mole, densities in moles per cc., pressures in normal atmospheres. R. M. S. denotes root mean square deviation.

Density Volume	T, °K. T, °C.	203.18 −70	223.18 −50	248.18 −25	273.18 0	293.18 20	323.18 50	373.18 100	473.18 200	573.18 300	R. M. S. deviations, %
0.0270	P obs.	775.81	860.45	961.88	1064.50	1145.76					
37.0370	% dev.	2.10	1.60	1.02	0.90	0.86					1.384
0.0245	P obs.	655.40	727.49	815.46	902.72	970.83	1072.24				
40.8163	% dev.	−0.24	−0.26	−0.28	−0.20	−0.24	−0.27				0.251
0.0220	P obs.	550.48	611.58	686.59	760.20	817.66	904.09	1048.55			
45.4545	% dev.	−0.53	−0.48	−0.39	−0.34	−0.41	−0.38	−0.19			.403
0.0195	P obs.	458.04	509.50	572.14	633.53	682.29	754.78	874.40			
51.2821	% dev.	−0.61	−0.44	−0.35	−0.34	−0.31	−0.29	−0.29			.390
0.0170	P obs.	376.29	418.73	470.13	520.89	561.25	621.67	720.07	914.70		
58.8235	% dev.	−0.52	−0.30	−0.24	−0.18	−0.13	−0.02	−0.10	−0.30		.267
0.0145	P obs.	304.03	338.21	379.26	420.48	452.73	501.74	582.06	740.40	892.28	
68.9655	% dev.	−0.20	0.03	−0.01	0.10	0.07	0.21	0.24	0.10	−0.65	.257
0.0120	P obs.	239.44	266.04	298.04	330.29	355.43	394.03	457.38	582.40	703.92	
83.3333	% dev.	−0.12	0.07	−0.02	0.07	−0.01	0.16	0.23	0.14	−0.35	.166
0.0095	P obs.	181.20	200.83	224.84	248.98	267.82	296.75	344.49	438.80	531.62	
105.263	% dev.	−0.08	−0.02	−0.09	−0.02	−0.12	0.02	0.12	0.06	−0.21	.100
0.0070	P obs.	128.13	141.66	158.40	175.21	188.45	208.58	242.01	308.15	374.10	
142.857	% dev.	0.01	−0.03	−0.09	−0.05	−0.11	−0.03	0.07	0.02	−0.02	.058
0.0045	P obs.	79.38	87.55	97.72	107.92	116.06	128.28	148.67	189.13	229.57	
222.222	% dev.	0.09	0.01	−0.06	−0.05	−0.05	−0.02	0.05	0.02	0.02	.048
0.0020	P obs.	34.13	37.56	41.84	46.13	49.56	54.70	63.29	80.37	97.50	
500.000	% dev.	0.09	0.04	−0.01	−0.02	−0.01	0	0.04	0.01	0.05	.040
R. M. S. deviations %		.706	.537	.366	.321	.318	.193	.163	.135	.315	

Summary

Bartlett and his collaborators have recently extended their P–V–1' measurements on hydrogen to include nine temperatures in the interval −70 to 300°, up to 1000 atmospheres. Their measurements and compilation of data from other sources have been smoothed and averaged and placed in a table (Table I) showing PV at even temperatures and pressures over that range. It is now possible to subject an equation of state for hydrogen to a severe test and to ascertain its limitations. The writers find the constants for hydrogen to be

Below the critical density: $A, = 124040$ $B_0 = 20.22$
$a = 56.18$ $b = -7.22$ $c = 20 \mathrm{X} 10^6$

Above the **critical** density: $A, = 124040$ $B_0 = 17.50$
$a = 56.18$ $b = -19.68$ $c = 20 \times 10^6$

in units of moles, atmospheres and cubic centimeters, for the Beattie–Bridgeman equation of state

$$PV^2 = RT(V + B_0(1 - b/V))\ (1 - c/VT^3) - A_0(1 - a/V)$$

A method of curve fitting was used which insures that trends and measurements be reproduced as faithfully as the formula is capable of doing. With the constants given above, over the temperature range −70 to 300°, the equation reproduces pressures with a root mean square error of 0.251% at 0.0245 mole per cc., the maximum being −0.28% at −25°; and with a root mean square error of 1.38% at 0.0270 mole per cc., the maximum being 2.10% at −70°; and almost perfectly at densities lower than these two. Thus the equation with the above constants reproduces trends and measurements satisfactorily at temperatures as low as −70° up to 0.0270 mole per cc. At densities greater than 0.0270 mole per cc. the calculated pressures (not shown in the table) are invariably too small and the deviations become quite large.

A break between high and low densities comes at about the critical density and is indicated by the intersection of the two lines in the graph of B vs. ρ. It may signify some sort of a change in the properties of hydrogen at this density.

The negative values of ϕ that occur at densities above 0.0180 mole per cc. are evidence for the predominance of repulsive forces between molecules at high densities.

WASHINGTON, D. C.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE ACTIVITY COEFFICIENTS AND THE ADSORPTION OF ORGANIC SOLUTES. I. NORMAL BUTYL ALCOHOL IN AQUEOUS SOLUTION BY THE FREEZING POINT METHOD

BY WILLIAM D. HARKINS AND ROY W. WAMPLER

RECEIVED AUGUST 2, 1930 PUBLISHED MARCH 6, 1931

I. Introduction

Since, when this work was begun, no determinations of the activity coefficients of organic solutes in dilute solution had been made, it seemed important to determine the activities for at least one typical organic solute. Since the activity coefficients are essential for the calculation of the adsorption in the surface of the solution, it was advisable to choose a substance for whose aqueous solutions the surface tension values are known. The substance used, n-butyl alcohol, has the further advantage that it can be purified with relative ease.

In the more concentrated solutions (0.25 molal and above) the results may be compared with those of Jones and Bury[1] on the organic acids, including butyric acid.

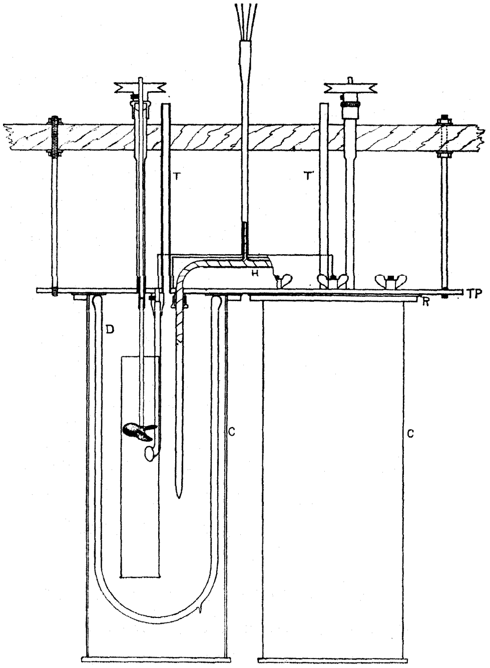

Fig. 1.

II. Freezing Point Apparatus

The freezing point apparatus (Fig. 1) is a modification of that used by Adams[2] and by Harkins and Hall,[3] and resembles that of Randall and Vanselow.[4] Two one-liter Dewar vessels (D) are suspended from a gold-plated brass plate (TP), each in a brass cylinder (C). When in use these brass cylinders were kept immersed in ice in a metal box, which was well insulated thermally by wool felt.

A 24-junction copper–constantan thermel, made in halves of twelve junctions each, was used for the determination of the temperature difference between ice–water in one Dewar, and ice–solution in the other. Five No. 30 double silk covered constantan wires in parallel were soldered to a single No. 35 double silk covered copper

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[1] Jones and Bury, *Phil. Mag.*, [7] 4,841 (1927).

[2] Adams, THIS JOURNAL, 37,481 (1915).

[3] Hall and Harkins, *ibid.*, 38,2658 (1916).

[4] Randall and Vanselow, *ibid.*, 46,2418 (1924).

wire. Only extremely uniform constantan wire, as tested by the method of White,[5] was used. The dried thermel was made air tight and waterproof. The equation for the potential difference between its ends is: $E = 957.10\,t - 1.1646\,t^2 + 0.00115\,t^3$ (t = °C.). Its performance was tested by the determination of the lowering of the freezing point produced hy various small amounts of mannite in water, as was done by Hall and Harkins.

A Zeiss laboratory type interferometer, with an all glass 4-cm. cell, and a 2-cm. arid an 8-cm. cell, was used to determine the concentration of the solutions. The interferometer was inclosed in a long thermostat kept at **25** * 0.01". With the 4-cm. cell one interferometer scale division corresponds to approximately 0.00006 molal n-butyl alcohol. For the most dilute solutions the 8-cm. cell was used.

III. Preparation of Materials

The *n*-butyl alcohol was Eastman's best grade. It was first treated with sodium bisulfite. Then it was refluxed with 10% sodium hydroxide for four hours, the alcohol separated from the aqueous layer and washed several times with water to free the alcohol from the base. The remaining base was neutralized with hydrochloric acid, lime was added and the mixture allowed to stand overnight. The partly dried alcohol was again treated with freshly heated lime and refluxed for three hours. The third treatment with lime removed the last traces of water and the alcohol was distilled from the lime and collected in fractions. The alcohol was fractionated twice more, the first time from a distilling column 40 cm. long and finally from a more effective column.

The latter distilling apparatus consisted of a one-liter distilling hulb connected to the fractionating column by a ground-glass joint. The column was 1.6 meters tall and 28 mm. in diameter, and was filled with 6-mm. glass tubing cut in 6-mm. lengths. A layer of sheet asbestos was wrapped around the column, then No. 21 B. and S. gage nichrome wire, five to six turns to the inch, was wrapped over the asbestos. The windings were now covered with a single tightly wrapped layer of asbestos cord. When the heater coil was connected to the 110-volt circuit through a rheostat, the temperature could be controlled so that it just counteracted the heat lost by the vapors in mounting the column. At the top of the column, a small but very efficient condenser was connected by means of a side arm. The ratio of reflux to distillate could be controlled[6] by means of *a* capillary stopcock connected to the side arm. The n-butyl alcohol obtained boiled at 117.70 to 117.74' (corrected).

The ice used in the determinations was frozen in the following manner. Distilled water was placed in a heavily nickel-plated copper vessel, 5 by 51 cm. at the bottom, 7.6 by 51 cm. at the top and 41 cm. high, and boiled for thirty minutes to remove the dissolved air. The tight fitting cover was then placed on the vessel, which was immersed in an ice and salt mixture to freeze. Solutions were made with distilled water that had just been boiled and cooled.

The problem of the air dissolved in the water and the solutions was made difficult in this case since the solute is volatile. The removal of the dissolved air by evacuation of the freezing point apparatus as used by Randall and Vanselow did not give a stable condition of equilibrium. After evacuating for thirty to sixty minutes, the water and the solution both being practically free from dissolved air at the outset, air was admitted through a soda lime tube and after twenty to thirty minutes, readings were taken. The temperature rose in every case and continued to rise slowly for a period of two to three hours, equilibrium never being reached. The method of saturating the solutions with air as used by Rodebush and Hovorka[7] was not applicable, for the solubility of air in the

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[5] White, THIS JOURNAL, 36, 2292 (1914).

[6] Lovelace, *Ind. Eng. Chem.*, 18, 826 (1926).

[7] Rodebush and Hovorka, THIS JOURNAL, 47, 1617 (1925).

solutions is different from that in water, especially in the more concentrated solutions. Rodebush and Hovorka[7] make the statement that for salt solutions any error which might arise from this cause is less than the experimental error for solutions of 0.01 molal concentration. The method of removing dissolved air at the outset was adopted as the most advisable procedure.

IV. Experimental Procedure

The distilled water ice was cracked by crushing it through an iron grating. The finely divided ice was removed, leaving pieces from 7 to 10 mm. in diameter. The cracked ice was washed thoroughly with distilled water and finally twice with the distilled water that was used in making the solutions. Approximately 400 g. of ice was placed in each Dewar vessel and boiled distilled water was added so that the surface would be just 4 mm. above the edge of the stirrer tube. The top was placed in position and the apparatus placed in the ice thermostat. The stirrers were started and after about two hours readings were taken until no change in temperature was noted, thus showing that equilibrium had been established. In the meantime, the solution to be used was placed in an ice and salt mixture, where it was allowed to remain until ice started to freeze out. The water in the right-hand Dewar vessel was removed by suction and the solution was added to replace it. Stirring was continued for thirty to sixty minutes before readings on the potentiometer were taken. Thereafter, readings were taken every five minutes until four or five readings showed that equilibrium had been established. A sample of the solution was removed by suction directly into a 100-cc. volumetric flask. Ice water was added to replace the solution removed. By continuing in this manner, it was possible to make the determinations for as many as six to eight different concentrations in a day. As soon as the solutions were removed from the freezing point apparatus, they were brought to the correct temperature and their concentrations determined in the interferometer, thus avoiding any chance for evaporation or change in concentration due to any other cause. The more concentrated solutions were analyzed in two ways. First, they were checked against a solution of approximately the same concentration. Then, they were diluted by weight to a concentration around 0.04 to 0.05 molal and compared against the water used in making up the solutions.

V. Method of Calculation

The method of calculation of the activities is that given by Lewis and Randall.[8] The equation for the activity of the solute is

$$d \ln a_2 = \frac{d\vartheta}{\lambda m} + 0.00057 \frac{\vartheta d\vartheta}{m} \qquad (1)$$

In order to integrate the equation use is made of the quantity j which is defined by the equation

$$j = 1 - \frac{\vartheta}{\lambda m} \qquad (2)$$

which, when differentiated, gives

$$\frac{d\vartheta}{\lambda m} - \frac{\vartheta dm}{\lambda m^2} = -dj \qquad (3)$$

Substituting the value of ϑ/m derived from Equation 2 in Equation 3 and rearranging

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[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," 1st ed., McGraw-Hill Book Co., Inc., New York, 1923, p. 286.

$$\frac{d\vartheta}{\lambda m} = (1 - j)\, d \ln m - dj \tag{4}$$

Substituting in Equation 1 and subtracting d ln *m* from both sides

$$d \ln \frac{a_2}{m} = -j\, d \ln m - dj + 0.00057\, \frac{\vartheta d\vartheta}{m} \tag{5}$$

Integrating from infinite dilution up to a given molality

$$\ln \frac{a_2}{m} = \int_0^m -j\, d \ln m - j + 0.00057 \int_0^m \frac{\vartheta}{m}\, d\vartheta \tag{6}$$

By means of the appropriate graphs, the area under the curves is ascertained and thence the activities.

VI. Discussion of Results

In Table I are given the freezing points for the different concentrations of n-butyl alcohol. The third column gives the molal freezing point lowering ϑ/m. In the fourth and fifth columns are, respectively, the values of j and j/m, while the activities are found in the last column. The values of j/m were obtained from a smooth curve of a plot of j/m against the molality. A graph of the freezing point lowering ϑ/m against the molalities m is shown in Fig. 2.

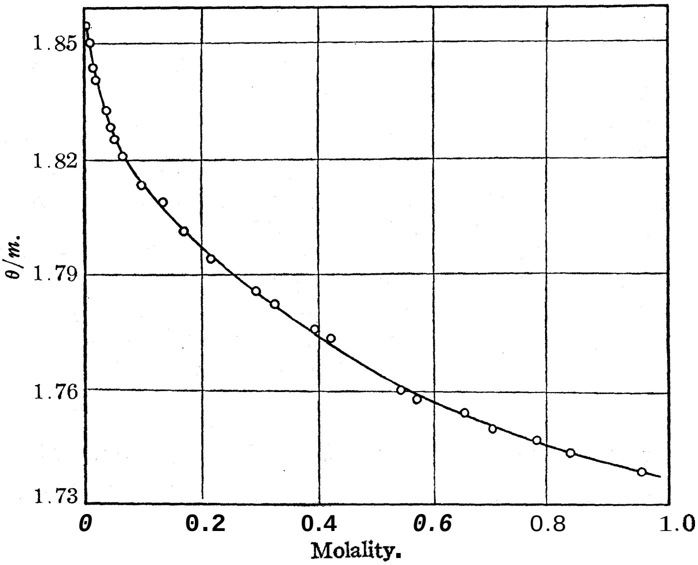

Fig. 2.—Molal freezing point lowering for n-butyl alcohol in water.

In Table II, the values of the activity coefficients are given for rounded values of the concentration. The values of the two integrals and $-j$ of Equation 6 are also given. The integral $\int_0^m - j\, d \ln m$ is designated as A.

TABLE I

LOWERING OF THE FREEZING POINT (ϑ) PRODUCED BY n-BUTYL ALCOHOL OF MOLALITY

m = Moles per 1000 g. of Water

m	ϑ	ϑ/m	j	j/m (interpolated)	a_2
0.95555	1.66128	1.7385	0.06428	0.0673	0.78711
.83881	1.46253	1.7436	.06158	.0725	.69802
,78227	1.26659	1.7469	.05932	.0760	.65472
.70353	1.23100	1.7497	.05830	.0804	,59362
,65318	1.14570	1.7540	.05595	.0842	.55428
.57148	1.00432	1.7574	.05416	.0916	,48982
.54338	0.95622	1.7598	.05287	.0941	,46748
.41966	.74425	1.7734	,04551	.1084	.36548
.39195	.69606	1.7759	,04420	.1128	.34492
.32265	.57504	1.7822	.04077	.1264	.28731
.29236	.52206	1.7857	.03892	.1331	,26187
,21532	.38634	1.7942	.03429	.1593	.19733
.16774	,30221	1.8016	.03032	.1837	.15452
,16409	.29556	1.8012	.03059	.1864	.15133
,13356	,24161	1.8091	.02636	,2076	.12434
.09748	.17680	1.8136	.02385	.2447	,09191
.08067	.14679	1.8195	,02062	.2686	.07657
,06894	.12554	1.8211	.01975	.2865	,06578
.06680	.12166	1.8211	.01986	.2928	,06381
.05206	.09505	1.8257	.01739	.3250	.05011
,05123	.09359	1.8269	.01674	.3268	,04933
.04631	,08470	1.8288	.01572	.3394	,04472
.03982	.07300	1.8332	.01430	.3590	,03859
.02420	,04452	1.8398	.00997	,4120	,02372
.019330	,035588	1.8411	.00832	.4304	,018999
,016049	,029569	1.8425	.00711	.4428	.015852
.014184	,026163	1.8445	.00638	.4488	.013999
.011403	,021116	1.8510	.00525	.4600	.011281
.004134	,007669	1.8550	.00201	.4870	.004117
.001027	.001818	1.7690	.00051	.4970	.001026

The directly calculated values of j/m are given in Figs. 4 and 5. The interpolated values are given above. At concentrations below 0.05 molal the mean difference between the two amounts to a temperature difference of about one fifty-thousandth of a degree.

while B represents the other integral $0.00057 \int_0^m \vartheta/m \, d\vartheta$. The activity coefficients γ, or a_2/m, are given in the fifth column (see Fig. **3** also).

The activity coefficient of butyl alcohol in its 1.0 molal solution (0.82) is approximately that of a 0.07 molal solution of potassium or sodium chloride. If the activity coefficient of butyl alcohol at 1 molal is considered to be unity, then that in a 0.25 *m* solution is 1.101, while the corresponding values of Jones and Bury are 1.160 for butyric, 1.091 for propionic, and 1.015 for formic acid. Thus the value for butyl alcohol is not very different from that for propionic acid. From this comparison it seems

TABLE II

VALUES OF THE ACTIVITY COEFFICIENT (a_2/m) OF n-BUTYL ALCOHOL IN ITS AQUEOUS SOLUTIONS

The values for the activity coefficient in the column marked (I) correspond to extrapolation along the heavy line, and (2) along the light line in Fig. 5.

Molelity m	$-A$	I	B	log a_2/m	Activity coefficient, a_2/m (1)	(2)
0.001	0.000499	0.00050	. . .	0 999566	0 9990	0.9991
,003	.001485	,00147	....	.998717	.9971	.9974
.006	.002946	.00288	.....	.997470	.9942	.9946
.010	.004840	,00465	0.00001	.995883	.9906	.9911
,020	.009308	.00856	,00004	.992246	.9823	.9833
,030	.013380	.01173	.00006	.989121	.9753	.9764
.040	.017100	,01432	.00008	.986389	.9691	.9702
,050	,020530	.01645	.00010	.983983	.9638	9650
,070	,026612	.01995	.00013	.979834	.9546	.9558
.100	,034442	.02416	00019	.974632	.9433	.9445
.150	,044273	.02928	00028	.967361	.9276	.9288
.200	.054196	.03342	.00038	.961943	.9161	.9173
.250	.062971	.03667	.00046	,957032	.9058	.9070
.300	,069911	.03926	,00054	,952986	.8974	.8986
.400	.082011	.04490	.00071	.945321	.8817	.8829
.500	.092521	.05015	.00089	.938570	.8681	.8693
.600	.101901	.05465	.00106	.932636	.8563	.8574
.700	.110401	.05790	.00123	.927627	.8465	.8476
.800	.118201	.06050	.00141	.923192	.8379	.8390
.900	.125401	.06290	.00158	,919130	.8301	.8312
1.000	.132101	.06530	.00175	.915242	.8227	.8238

TABLE III

FILMS OF BUTYL ALCOHOL ON WATER

Molality	Activity	Surface tension	Moles per sq. cm. × 10^{10}	Number of molecules per sq. cm. Adsorbed	Already present	Total	Area per molecule adsorbed	Area per molecule, sq. Å.	Square root of area
0.00329	0.00328	72.80							
.00658	.00654	72.26							
.01320	.01304	70.82	1.26	0.76	0.04	0.80	132	120	11
.0264	.02581	68.00	2.15	1.31	.06	1.37	76	73	8.8
.0536	.05184	63.14	3.54	2.14	.10	2.24	47	45	6.7
.1050	.09892	56.31	4.72	2.86	.15	3.01	35	33	5.8
.2110	.19277	48.08	5.26	3.19	.23	3.42	31.4	29.2	5.4
.4330	.37961	38.87	5.69	3.45	.37	3.82	29.0	26.2	5.1
.8540	.71189	29.87	6.03	3.65	.56	4.22	27.4	23.7	4.9

Surface tensions at 25". Activities at 0°. It is assumed that the relative activities at 25° are the same as at 0°.

probable that the activity coefficients of the acids vary somewhat more with the concentration than those of the alcohols, if the number of carbon atoms is the same.

TABLE IV

ADSORPTION AND MOLECULAR AREA FOR ORGANIC ACIDS

Temperature, 0°

Moles per 1000 g. of water	Area per molecule in Ångström units Adsorbed	In film
	Propionic Acid	
0.1008	70.8	63.8
.2420	47.2	41.8
1.0167	32.4	26.4
2.3110	28.8	21.7
	Butyric Acid	
0.0211	98.0	93.0
.0503	62.5	59.3
.1049	43.2	40.4
.2510	34.6	31.5
.5088	30.2	26.6
1.095	26.5	22.2

It has usually been considered that the value of the function j/m is constant below 0.1 molal but Fig. 4 shows that it increases rapidly as the molality decreases, and, on the whole, more rapidly at the lower concentrations. Figure 5 gives the values of j/m at molalities below 0.1 molal. The middle curve represents the smoothed values of j/m, while the upper and lower curves show the deviation produced in j/m by an error of 0.00005° in the temperature measurement. It is evident that the deviations from the mean are in general much less than a twenty-thousandth of a degree, and that below 0.05 molal the average deviation is about one fifty-thousandth of a degree.

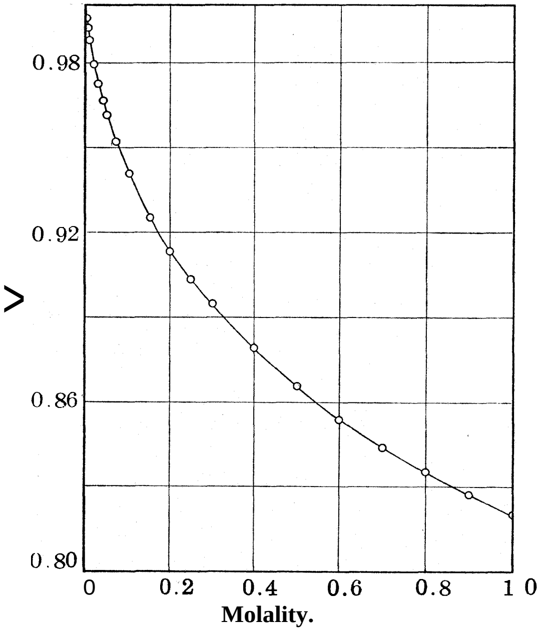

Fig. 3.—Activity coefficient of *n*-butyl alcohol in its aqueous solutions,

In Table II the activity coefficients under (1) represent the extrapolation to zero concentration along the heavy line of Fig. 5, which corresponds better to the data at the lowest concentrations, while those under (2) correspond to extrapolation along the light line, which seems better on the basis of the data at higher concentrations. The maximum difference produced in the activity is only 0.12%.

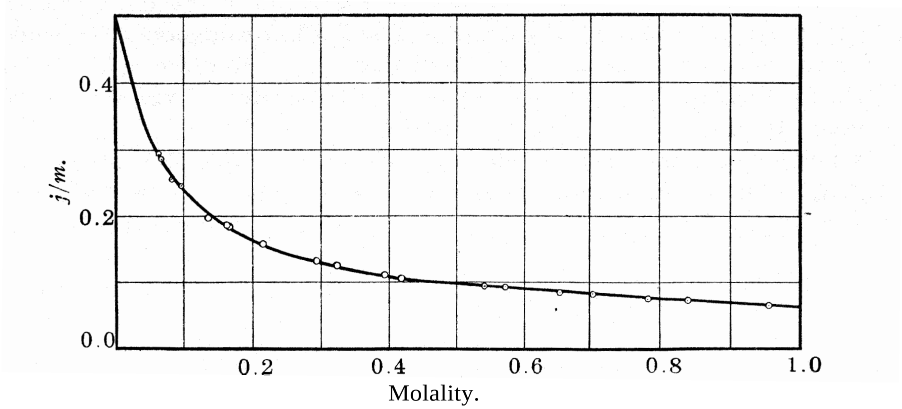

Fig. 4.—Variation of j/m with the molality of butyl alcohol.

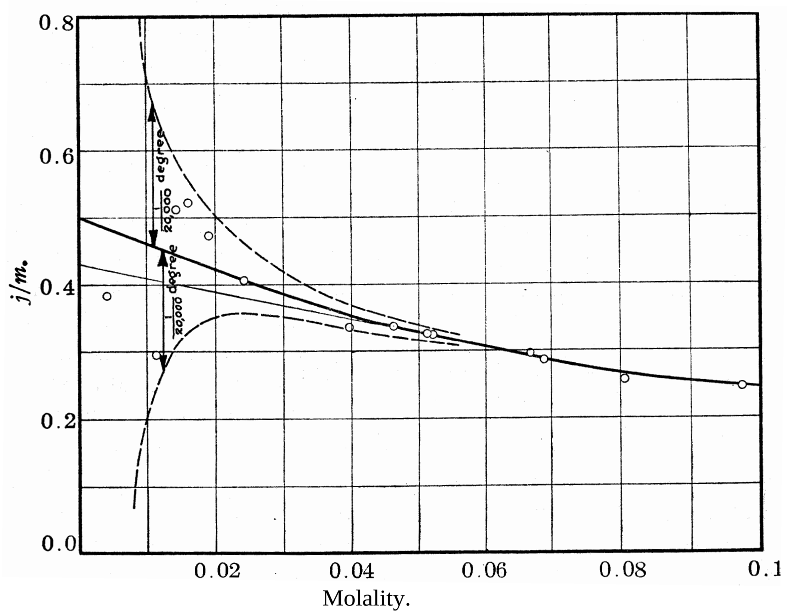

Fig. 5.—Variation of j/m with the molality of butyl alcohol.

VII. The Film of Butyl Alcohol on an Aqueous Solution

The adsorption (u) in the surface region of a solution is supposed to be given by the equation

$$u = -\frac{1}{RT}\frac{d\gamma}{d \ln a}$$

in which γ is the surface tension of the solution, a is the activity of the solute, T is the absolute temperature and R is the gas constant. Figure 6 gives the surface tension values for aqueous solutions of butyl alcohol as determined by King, plotted against the logarithm of the activity of the alcohol in its aqueous solutions as given earlier in this paper. The values for the adsorption, as calculated from these data are given in Table III. At the highest concentration (0.854 molal) the area of the surface per molecule adsorbed is 27.4 sq. Å. units of area.

The area per molecule for normal alcohols in insoluble films on water is about 21.6 sq. Å. units at zero compression. The value per adsorbed molecule of butyl alcohol (27.4) is about one-third larger, and this suggests that the film is monomolecular with respect to butyl alcohol.

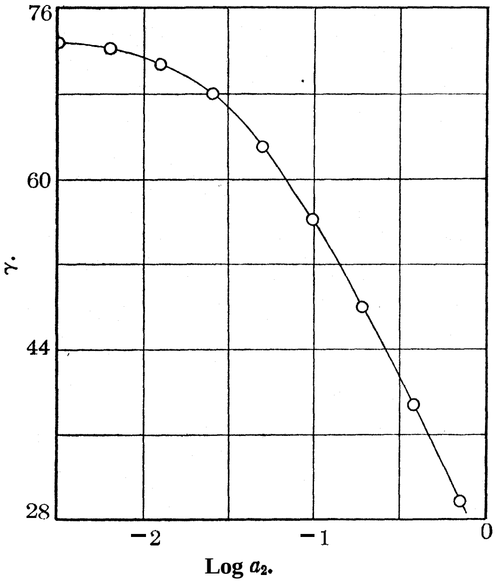

Fig. 6.—Surface tension and activity of butyl alcohol in water.

The value of the adsorption (u) in the above equation gives the number of moles of solute which must be added to the whole solution in order to keep the activity of the solute constant when the area of the surface of the solution is increased by one sq. cm. While it is evident that some solute is present in the surface film of a solution if the adsorption (u) is zero, sufficient attention has not been given to this fact. For example, the value of u for a 0.854 m solution of butyl alcohol is 3.65 × 10^{14} molecules per sq. cm. of increase of surface. It is commonly assumed that this number of alcohol molecules moves into the surface film. However, if the number of molecules of butyl alcohol in the surface were to be determined an infinitesimal time after the formation of the surface, the number would not be negligible. It may be assumed that a plane surface, one sq. cm. in area, inside such a solution would cut 0.56 × 10^{14} molecules of butyl alcohol, since this number is equal to the two-thirds power of the number of alcohol molecules in one cc. of the solution. It will be assumed that this is the number of alcohol molecules "initially" present in the first surface layer. If all of the adsorbed molecules move into this same "layer" the total number present is 4.22 X 10^{14}, and the area per molecule of alcohol present in this layer is 23.7 sq. Å. units, or very nearly that (21.6) exhibited by alcohol molecules in insoluble films. For comparison the surface tension data of Rehbinder and the activity data of Jones and Bury have been used to calculate the corresponding areas for propionic acid and butyric acid (Table IV). The minimum areas are 21.7 and 22.2 sq. Å., respectively. The first surface layer of solute molecules, as defined in this paper, does not include the entire surface region as defined in earlier papers by Harkins. The relation between the first surface layer, sometimes called the surface film, and the surface region, will be discussed in a later paper.

Summary

1. The activity values for solutions of n-butyl alcohol in aqueous solution were determined by the use of a specially designed apparatus for the determination of the lowering of the freezing point. This was a modified form of the apparatus used by Adams, and by Harkins and Hall. It was sensitive to 0.00001° when used with a White double combination potentiometer.

2. The n-butyl alcohol was purified carefully in a specially designed fractionating column. The material used distilled over within a range of 0.04°.

3. The activity coefficient of n-butyl alcohol in its 1 molal solution is 0.8227. At 0.5 M it is 0.8681, and at 0.1 M, 0.9433. Thus the deviation from normal behavior is of considerable magnitude with this organic solute. This indicates that the concentration of the solution cannot be used in place of the activity, in accurate calculations. It may be assumed that the deviations produced by the $-$COOH group are somewhat larger and other active groups of this type give deviations of about the same general order of magnitude.

4. If the "adsorption equation" is correct, the film of butyl alcohol on its aqueous solutions is monomolecular. The area per molecule of alcohol in the film is 23.7 sq. Å., while the well-known value for longer alcohol molecules in insoluble films is 21.6 sq. Å.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE BEATTIE–BRIDGEMAN EQUATION OF STATE AND BARTLETT'S P–V–T DATA ON A 3:1 HYDROGEN–NITROGEN MIXTURE

BY W. EDWARDS DEMING AND LOLA E. SHUPE

RECEIVED SEPTEMBER 25, 1930 PUBLISHED MARCH 6, 1931

Direct Determination of the Constants

In previous papers[1] the constants for the Beattie–Bridgeman[2] equation of state have been published for the high pressure data obtained at this Laboratory with nitrogen and hydrogen. We now present constants determined by the same method for a 3:1 hydrogen–nitrogen mixture, the experimental data for which were published by Bartlett and his collaborators[3] who record their own measurements from −70 to 300° up to 1000 atmospheres, and a few scattered ones taken from the work of Verschoyle. After comparing the observed pressures in the table with pressures calculated using the constants to be given in Equation 6, we shall study the schemes for combining the constants previously found for hydrogen and nitrogen to devise constants for the mixture.

To settle on a value for the ratio of PV at 0° and 0 pressure to PV at 0° and 1 atm., we took the weighted average of the best values[4] known to us for hydrogen and nitrogen, which are 0.99939 and 1.00046. The weighted average is $(3 \times 0.99939 + 1.00046)/4 = 0.99966$. Using Birge's value[6] 22414.1 cc. for the volume of a mole of an ideal gas at S. T. P. we have 22421.7 cc. for the volume of a mole of the 3:1 mixture at S. T. P. Bartlett expresses his PV with $PV = 1$ at S. T. P., so we multiply his specific volumes by 22421.7 to change them into cc. per mole. We use $R = 82.0489$ cc. atm. per mole per degree, and 273.18°K. for the ice point, as given by Birge.

As we mentioned in our paper on hydrogen, the three lowest temperatures in Bartlett's table should have been published as −69.90, −49.93, −24.99° instead of −70, −50, −25°. We have made these slight corrections and have interpolated to integral temperatures in our process of smoothing.[6] The pressures at integral temperatures and densities derived from Bartlett's publications are listed in the table later on. The extrap-

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[1] Deming and Shupe, THIS JOURNAL, 52, 1382 (1930); 53, 843 (1931).

[2] Beattie and Bridgeman, Proc. Am. Acad. *Arts and Sci.*, 63, 229 (1928); THIS JOURNAL, 49, 1665 (1927); and later papers.

[3] Bartlett, Cupples and Tremearne, *ibid*, 50, 1275 (1928); Bartlett, Hetherington, Kvalnes and Tremearne, *ibid.*, 52, 1363 (1930).

[4] "International Critical Tables," Vol. III, p. 3.

[5] Birge, Phys. *Rev.* Supplement, 1, 1 (1929).

[6] Described in the preceding paper,

olations beyond 1000 atm. seemed to us reliable, judging from the perfect regularity of the ρ, Δ isotherms after the process of smoothing. The extrapolations were made by extending the ρ,Δ curves. The nearness of the experimental points to these curves, which are greatly magnified deviation curves, attests to the high precision of the experimental work.

Throughout this paper the notation will be the same as that in the papers on nitrogen and hydrogen, and the equations, tables, and figures will be numbered from the last ones in the paper on hydrogen.

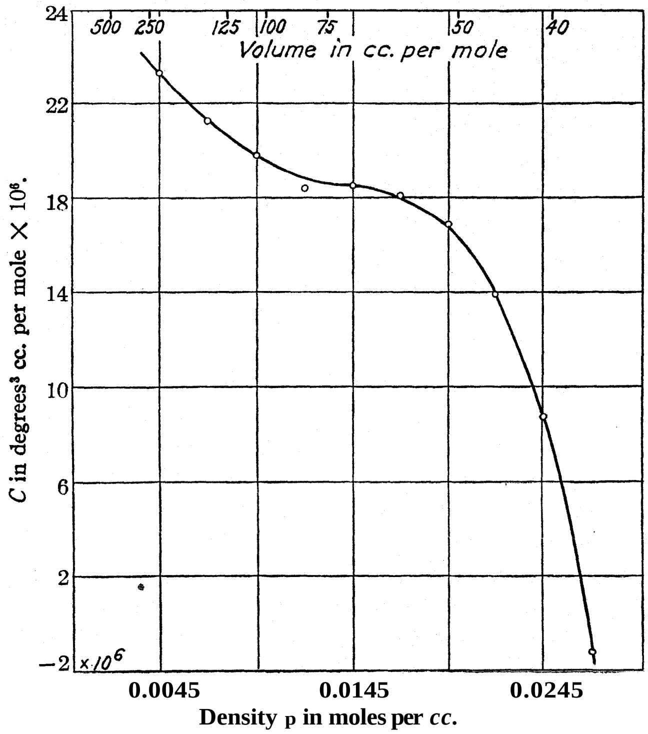

Fig. 2.—The values of c that render $\Sigma[(P_{\text{obs.}} - P_{\text{calcd.}})/P_{\text{obs.}}]^2$ an absolute minimum at each density of the 3:1 hydrogen–nitrogen mixture.

Attempts to find the best value of c revealed immediately some peculiarities of this mixture. The best value of c for $\rho = 0.0270$ mole per cc. turned out to be negative; and the values found for the next three densities were so discordant that we finally computed c for every density. The graph of c vs. ρ (Fig. 2) shows these peculiarities. We chose $c = 16 \times 10^6$ as likely to give the best results over the whole range. The rather long extrapolations beyond 1000 atm. at the low densities and high temperatures are not responsible for the peculiar behavior depicted by the graph;

the calculations were repeated with the extrapolated pressures discarded and the resulting graph showed c to be a trifle more variable than before.

The tendency for c to decrease and finally to become negative as the density increases seems to be related to the similar tendency exhibited by ϕ with hydrogen and to a smaller extent, as will be seen, with this mixture. An explanation for this behavior is found in the existence of repulsive forces that come into play at high densities.[7] The same might have been found true with nitrogen if that work had included higher densities.

The values of ψ and ϕ with $c = 16 \times 10^6$ that render the mean square per cent. deviations of the calculated pressures a minimum along each isochore were found and were then used to compute $B = (\psi V^2 - RV)/R$ and $A = \phi V^2$ at each density. The graphs of A and B as functions of ρ are shown in Fig. **3.** There is little doubt that two lines for each are indicated; the locations finally selected are shown in the figure, and their slopes and intercepts determine A_0, a, B_0, b.

These pairs of lines intersect at 0.0137 and 0.0132 mole per cc. Now this mixture probably has a critical density in this vicinity. In general the critical curve for a binary mixture is fairly smooth between the two components. The "International Critical Tables" give 0.0154 and 0.0111 mole per cc. for the critical densities of hydrogen and nitrogen; so the critical density of the mixture probably lies in the neighborhood of 0.014 mole per cc. The intersections in Fig. **3** are close to this value. We found the same with hydrogen in the preceding paper. It appears that the equation of state has one set of constants below the critical density, and another set above it. This behavior may be common to all gases; our work on nitrogen barely included the critical density, so we cannot predict its behavior. Figure 2 shows a peculiar flattening of the c vs. ρ curve in the interval $0.0120 < \rho < 0.0145$, which may be related to the breaks in the A and B plots. We are indebted to Professor Beattie for pointing out to us the possible connection between the breaks in the A and B plots and the critical density of the mixture.

From Fig. **3**

$$\left.\begin{array}{lll}
\multicolumn{3}{l}{\text{Below the critical density}} \\
A_0 = 3000 \times 10^2 & & B_0 = 25.03 \\
a = 21.36 & b = -15.16 & c = 16 \times 10^6 \\
\multicolumn{3}{l}{\text{Above the critical density}} \\
A_0 = 3489 \times 10^2 & & B_0 = 21.42 \\
a = 28.56 & b = -30.58 & c = 16 \times 10^6
\end{array}\right\} \qquad (5)$$

in units of moles, atmospheres, and cubic centimeters.

Table III lists the smoothed pressures at even temperatures and densities and the comparison with the calculated pressures.

Consideration of the deviations in Table III shows that the equation of

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[7] Deming and Miss Shupe, an article to appear.

state with the constants of Equations 5 reproduces pressures almost within the experimental error up to 0.0270 mole per cc.; at this density the root mean square deviation is 1.8%.

The Constants Determined by Combination.—A scheme for computing analytically the P–V–T relations of a mixture from those of the constituents would be valuable. In recent papers Beattie and others[8] have given histories of the different devices for making such calculations, and have investigated the result of combining the constants in the equations of state for the constituents to get constants to be used for the mixture. Beattie and Ikehara have made an exhaustive study of this idea using the Beattie-Bridgeman equation of state. They combined a, b, c, $\sqrt{A_0}$ linearly by mole fraction, and compared three methods of combining B_0-linear, Lorentz, and linear square root. We propose here to extend this study to the high pressure data on the 3:1 hydrogen–nitrogen mixture.

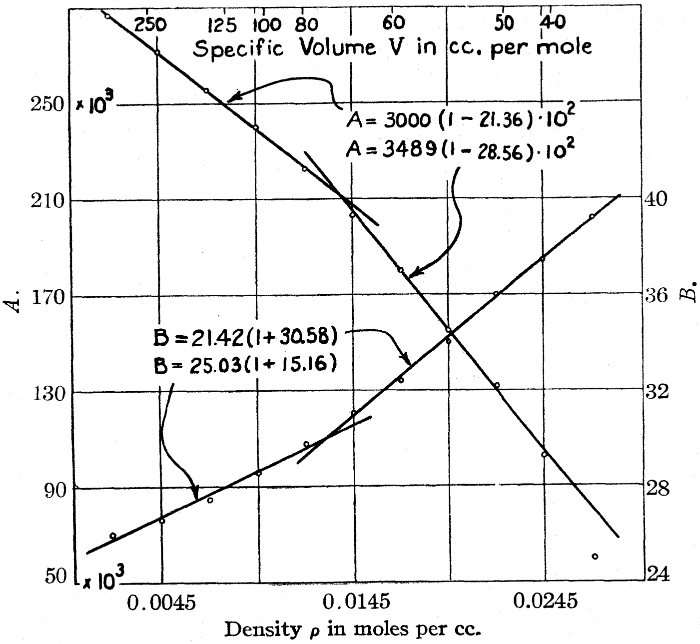

Fig. 3.—The A and B plots for the 3:1 hydrogen–nitrogen mixture.

Suppose B_{oh} and B_{on} are the B_0 constants for hydrogen and nitrogen, and that these two gases are present in a binary mixture to the extent of mole fractions x_h and x_n; then the B_0 constant for the mixture (B_{ox}) will be formed quadratically:

$$B_{ox} = B_{oh}x_h^2 + 2B_{hn}x_hx_n + B_{on}x_n^2 \qquad (6)$$

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[8] Beattie, This Journal, 51, 19 (1929); Beattie and Ikehara, *Proc. Am. Acad. Arts Sci.*, 64, 127 (1930); Keyes and Burks, This Journal, 50, 1100 (1928).

TABLE III

OBSERVED PRESSURES AS SMOOTHED FROM THE COMPILATION OF BARTLETT FOR 3:1 HYDROGEN–NITROGEN MIXTURE

Comparison with pressures calculated from the Beattie–Bridgeman equation of state, using the constants of Equation 5. Volumes are in cc. per mole, densities in moles per cc., pressures in normal atmospheres. R. M. S. denotes root mean square.

Density volume	T, °K. T, °C.	203.18 −70	223.18 −50	248.18 −25	273.18 0	298.18 25	323.18 50	373.18 100	473.18 200	573.18 300	R. M. S. dev., %
0.0270	P obs.	840.34	938.41	1057.48	1176.10	1296.30	1420.35				
37.0370	% dev.	2.49	2.11	1.08	1.41	1.45	1.81				1.790
0.0245	P obs.	690.12	772.89	874.87	975.98	1076.01	1177.69	1376.34			
40.8163	% dev.	0.23	0.06	−0.04	−0.05	−0.06	0.13	0.19			0.129
0.0220	P obs.	566.21	634.84	720.10	803.70	886.61	970.95	1136.43	1461.07		
45.4545	% dev.	0.12	0.01	0.04	−0.01	−0.04	0.15	0.25	0.11		.120
0.0195	P obs.	461.75	518.10	587.71	657.22	725.28	792.84	929.77	1196.11	1462.84	
51.2821	% dev.	−0.24	−0.30	−0.30	−0.20	−0.23	−0.28	−0.06	−0.26	−0.29	.250
0.0170	P obs.	373.11	419.02	475.11	531.39	586.95	641.41	751.74	969.18	1185.21	
58.8235	% dev.	−0.26	−0.20	−0.25	−0.14	−0.10	−0.20	−0.09	−0.16	−0.25	.192
0.0145	P obs.	297.98	334.28	379.18	423.33	467.19	511.04	598.80	772.57	945.55	
68.9655	% dev.	0.19	0.22	0.27	0.23	0.20	0.20	0.28	0.27	0.02	.222
0.0120	P obs.	233.27	260.77	295.70	329.78	363.29	397.43	465.13	599.89	731.96	
83.3333	% dev.	0.23	0.11	0.30	0.27	0.14	0.21	0.27	0.32	0.02	.222
0.0095	P obs.	176.05	196.20	222.17	247.26	272.07	297.23	347.20	446.86	545.33	
105.263	% dev.	−0.09	−0.24	−0.06	0.00	−0.11	−0.06	−0.04	−0.01	−0.17	.114
0.0070	P obs.	124.74	138.58	156.28	173.70	190.88	208.13	242.46	311.15	379.61	
142.857	% dev.	−0.16	−0.29	−0.08	−0.04	−0.10	−0.10	−0.14	−0.14	−0.17	.152
0.0045	P obs.	77.78	86.11	96.61	107.14	117.55	127.92	148.52	189.91	231.36	
222.222	% dev.	−0.03	−0.13	−0.07	0.03	0.03	0.01	−0.09	−0.10	−0.06	.074
0.0020	P obs.	33.79	37.25	41.59	45.96	50.30	54.61	63.22	80.47	97.78	
500.000	% dev.	0.04	0.00	0.01	0.09	0.11	0.09	0.02	−0.01	0.04	.059
R. M. S. deviations %[a]		0.179	0.188	0.183	0.112	0.127	0.156	0.171	0.185	0.163	

[a] Density 0.0270 is excluded from these R. M. S. deviations.

The three methods mentioned above apply to the interaction factor B_{hn}, thus

$$\text{By the linear method, } B_{hn} = {}^1/_2(B_{oh} + B_{on}) \quad (7)$$

$$\text{By the Lorentz method, } B_{hn}^{1/3} = {}^1/_2(B_{oh}^{1/3} + B_{on}^{1/3}) \quad (8)$$

$$\text{By the linear square root method, } B_{hn}^2 = B_{oh}B_{on} \quad (9)$$

We shall use subscripts h and n for hydrogen and nitrogen; then $x_h = {}^3/_4$ and x, $= {}^1/_4$, since our specific volumes are in cc. per mole.

If we combine the constants for hydrogen and nitrogen that were found to hold for densities below critical, the synthetic constants cannot be expected to hold above the critical density of the mixture. For nitrogen we found

$$\left.\begin{array}{lll} A,, = 1254 \times 10^3 & & B_{on} = 46.045 \\ a, = 18.68 & b_n = -25.88 & c_n = 61.64 \times 10^6 \end{array}\right\} \quad (10)$$

These have been changed to units of moles, atmospheres, and cubic centimeters. From Equation 3

$$\left.\begin{array}{lll} A_{oh} = 1240 \times 10^2 & & B_{oh} = 19.90 \\ a_h = 56.18 & b_h = -10.72 & c_h = 20 \times 10^6 \end{array}\right\} \quad (11)$$

Combination of 10 and 11 gives

$$\left.\begin{array}{ll} A_{om} = 2889 \ X \ 10^2 & a, = 46.80 \\ b_m = -14.51 & c_m = 30.41 \ X \ 10^6 \end{array}\right\} \quad (12)$$

$$\text{By the linear method, } B_{om} = 26.43 \quad (13)$$

$$\text{By the Lorentz method, } B_{om} = 25.76 \quad (14)$$

$$\text{By the linear square root method, } B_{om} = 25.42 \quad (15)$$

Pressures were calculated with these constants and compared with the observed pressures listed in Table III. The root mean squares of the deviations were taken with respect to temperature, and with respect to density for the five densities below critical. The most comprehensive presentation of these deviations seemed to be the graphical one in Figs. 4 and 5. Root mean square deviations for the pure gases using Equations 3 and 10, and for the 3:1 mixture using Equations 5 are shown for comparison.

The graphs fail to give information in two respects: they do not tell whether the deviations at a particular density are predominantly positive or negative, and they do not tell the extent of variation among the deviations at a particular density or temperature. Two general statements cover these points. At any one density the deviations for any one gas are roughly of the same magnitude, so unless they are nearly zero it is possible to state that they are either predominantly positive or predominantly negative. The deviations at all the densities within the range shown might be expected to be predominantly of the same sign. This is the case; they all turned out to be predominantly negative for all three methods of combination.

Here the linear square root method seems to be a little better than the other two, but none of them are satisfactory except at the lowest densities. The representation of data by the linear square root method of combination for B_0 is almost within the experimental error to densities as high as 0,0070 mole per cc., where, as can be seen in Fig. 4, the R. M. S. deviation is 1.17%.

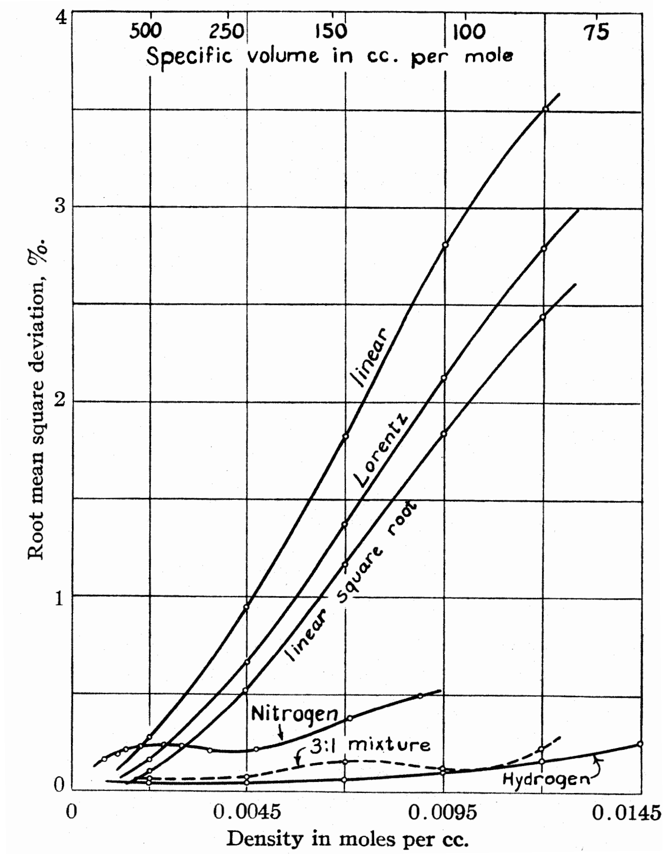

Fig. 4.—Root mean square deviations of pressures calculated by three methods of combining the B_0 constant, taken over the nine temperatures.

This is a different conclusion from that reached by Beattie and Ikehara, who say: "On the whole, linear combination for B_0 was slightly favored over the Lorentz method, while the linear square root relation gave the least satisfactory results. . . . Linear combination for each of the constants R, $\sqrt{A_0}$, a, B_0, b, and c of the Beattie–Bridgeman equation of state gives a satisfactory over-all correlation of the compressibility data on gas mixtures, although in some cases the representation of the data may not be within the experimental error."

A 3:1 hydrogen–nitrogen mixture was only one of many studied by

Beattie and Ikehara; their Fig. 15 shows percentage deviation *vs.* pressure at 0° up to 200 atmospheres for linear and Lorentz combination, using Verschoyle's data. Comparing their results as read from their Fig. 15 with our calculations, we find that our deviations by the linear and Lorentz methods are a little larger than theirs, but our results by the linear square root method are better than either their linear or Lorentz combinations.

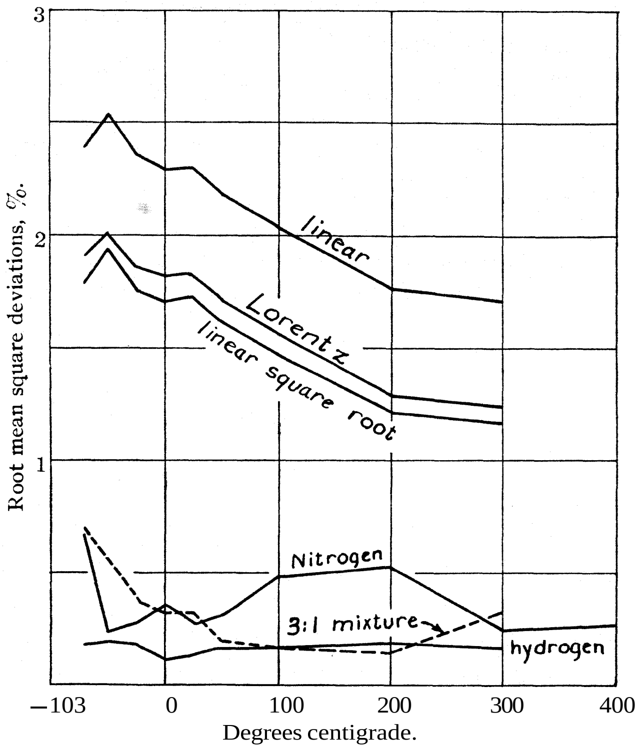

Fig. 5.—Root mean square deviations of pressures calculated by three methods of combining the B_0 constant, taken over the five densities below critical.

One might expect our deviations to be larger since our constants were determined for each constituent up to the critical density at each temperature. The constants that Beattie and Ikehara combined were determined for comparatively low densities, and their combination might be expected to fit the 3:1 mixture quite well at not too high pressures.

It should be noted that the data that we have used for the constituents and their mixture should be consistent, since Bartlett's work was all done with the same apparatus, and his measurements naturally received the most weight in the smoothing and averaging because he covered such a wide range of temperature and pressure.

Summary

Bartlett and his collaborators have recently extended their P–V–T measurements on a 3:1 hydrogen–nitrogen mixture to include nine temperatures in the interval –70 to 300°, up to 1000 atmospheres. A few observations from the work of Verschoyle were used with Bartlett's in a process of smoothing and averaging, in which interpolations and extrapolations were made to even densities from 0.0020 to 0.0270 mole per cc. and at even temperatures from –70 to 300°.

The writers have calculated the constants in the Beattie–Bridgeman equation of state

$$PV^2 = RT(V + B_0(1 - b/V))\,(1 - c/VT^3) - A_0(1 - a/V)$$

by two methods: (1) direct determination, and (2) combination of constants previously found for the constituents of the mixture. As with hydrogen, they find breaks in the plots of A and B vs. p in the region where one would expect the critical density to lie, namely, about 0.0135 mole per cc. By direct determination

$$\left.\begin{array}{lll}
\textbf{Below the critical density} & & \\
A_0 = 3000 \times 10^2 & & B_0 = 25.03 \\
a = 21.36 & b = -15.16 & c = 16 \times 10^6 \\
\textbf{Above the critical density} & & \\
A_0 = 3489 \times 10^2 & B_0 = 21.42 & \\
a = 28.56 & b = -30.58 & c = 16 \times 10^6
\end{array}\right\} \quad (5)$$

in units of moles, atmospheres, and cubic centimeters. Pressures calculated with these constants agree with the observed pressures within a few tenths of a per cent. up to 0.0270 mole per cc.; at this point the calculated pressures are all too low with a root mean square deviation of 1.8%. At any density, the fit is about as good at one temperature as at another.

For studying the combination of the constants of the constituents to derive constants for the mixture, a, b, c, $\sqrt{A_0}$ for hydrogen and nitrogen at densities below critical were combined linearly. The B_0 for each were combined in three different ways, namely, by the linear, Lorentz and linear square root methods. The deviations of pressures calculated with these synthetic constants increase rapidly as the density increases. Of the three, the linear square root method comes the nearest to being satisfactory; it reproduces pressures with a root mean square error of 1.17% at 0.0070 mole per cc., so it can be trusted to reproduce the P–V–T relations almost within the experimental error up to this density.

This conclusion disagrees with that recently published by Beattie and Ikehara, who state that the linear square root method is not as good as the other two. It is pointed out that the conclusions differ because of the different ranges of pressure and temperature that were used for determining the constants of the pure gases.

The peculiarity in the c *vs.* ρ graph (Fig. *2)* exhibiting the tendency for c to decrease and finally become negative as the density increases is believed to be related to the similar tendency of ϕ with hydrogen, and both are evidence for the predominance of repulsive forces between molecules at high densities.

WASHINGTON, D. C.

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

FLAME TEMPERATURES OF HYDROCARBON GASES[1]

BY G. W. JONES,[2] BERNARD LEWIS,[3] J. B. FRIAUF[4] AND G. ST. J. PERROTT[5]

RECEIVED OCTOBER 22, 1930 PUBLISHED MARCH 6, 1931

In a previous report by Loomis and Perrott[6] methods were described and results given for the flame temperatures of methane, propane, carbon monoxide and natural gas. They tried several methods for measuring the temperatures of stationary flames, details of which are given in the report mentioned. The spectral-line reversal method was finally adopted for the measurement of the flame temperatures of combustible gases, because after the apparatus has been properly calibrated and standardized, a large number of determinations may be made easily, accurately and quickly. This method was first used by Kurlbaum,[7] subsequently modified by Kurlbaum and Schulze,[8] and later by Fery.[9] More recently, Henning and Tingwaldt[10] used the method to measure the maximum temperature of the acetylene–oxygen flame, 3100°. Griffiths and Awbery[11] have also described this method and investigated its limitations and factors affecting the accuracy of the results obtained. Tests made by them to determine the influence of flame thickness on the observed flame temperatures showed that within the limits of $^1/_2$ inch to *2* inches, thickness is immaterial to the result, but to ensure sensitivity it is advisable to employ a thick flame. They also investigated the distribution of temperature from base to tip of the flame. The results showed a relatively uniform temperature

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[6] A. G. Loomis and G. St. J. Perrott, *Ind. Eng. Chem.*, 20,1004 (1928).

[7] Kurlbaum, *Physik. Z.*, 3, *332* (1902).

[8] Kurlbaum and Schulze, Ber. *deut. phys. Ges.*, *5*,*428* (1903).

[9] Fery, *Compt. rend.*, 137,909 (1903).

[10] Henning and Tingwaldt, Z. *Physik*, 48, *805* (1928).

[11] E. Griffiths and J. H. Awbery, *Proc.* Roy. *Soc.* (London), A123, 401 (1929)

in the lower region of the flame, followed by a very rapid decrease from this zone of uniform temperature as the tip of the flame is approached. They used this method for determining the maximum temperatures in gaseous explosions, for the measurement of the temperatures of stationary flames, using carbon monoxide and air at various ratios and rates, also for the measurement of the temperatures of flames of atomic hydrogen. It is of interest to note that values for the maximum flame temperatures of carbon monoxide–air mixtures varied over a range of 100° with the quantity of mixture burned in a given interval of time. The larger the quantity burned the higher the flame temperature for a given air–gas ratio at a given distance above the burner port. This is equivalent to lowering the point of measurement while keeping the rate constant. The temperatures found at the higher rates appear to approach a constant value. It is, therefore, necessary to burn a sufficient quantity of gas in unit time to ensure measuring the maximum temperature at **a** given constant distance above the burner.

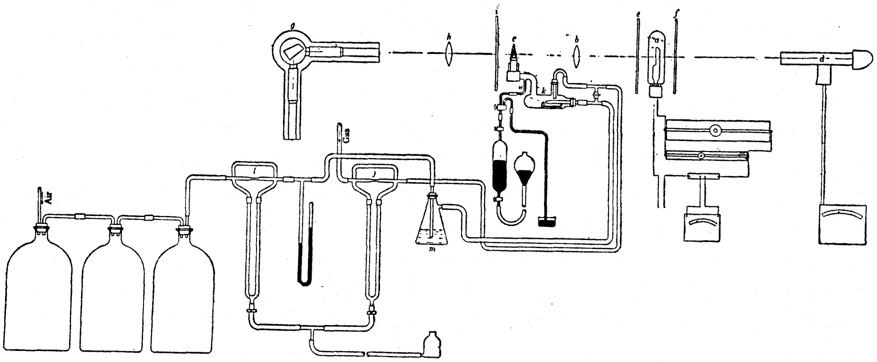

Fig. 1.—Apparatus for determining flame temperatures of gases.

In the spectral-line reversal method employed for obtaining the temperatures given in this report, use was made of a tungsten band lamp as a source of continuous radiation. Figure 1 is a diagrammatic sketch of the apparatus. The tungsten band lamp *a* was heated by a storage battery, the current input being controlled by variable resistances Light from the band lamp was focused by means of the lens b into the center of the flame c just above the tips of the inner cones. The brightness temperature of the band lamp was read by means of the optical pyrometer *d*, of the disappearing filament type, the screens *e* and f permitting radiation to emerge from the same point on the heated band. The optical pyrometer recorded the same temperature (within 5°) on both sides of the band lamp. Furthermore, there was no evidence of a **temperature** gradient one centimeter either side of the center of the band. The image of the heated tungsten band together with the flame was focused on the slit of the spectrometer g by means of the lens h. **A** screen *i* permitted radiation from an area of the flame equal to the area of the band image to reach the spectrometer. The flame was colored by means of sodium, lithium, or thallium salts. The spectral lines (for sodium, the resonance doublet XX = 0.5890–0.5896μ) are seen as bright lines upon the continuous spectrum from the band lamp if the latter is cooler than the flame, but if it is hotter the bright lines are reversed and appear dark upon the brighter background of the continuous spectrum of the band lamp. Final adjustment was made by the observer at the eyepiece of the spectrometer. When the lines are just completely reversed the brightness temperature of the tungsten band lamp is the same as the temperature of the flame. At **this** point the former temperature was determined by means of the optical pyrometer.

Experimental Part

Burners Used **in** Investigation.—Three types of burners were used in our investigation. These are shown in Fig. 2. Type **A** consisted of a small brass box 5.5 by 3.5 by **3.5 cm.** Protruding through the top of the box were fifteen **quartz** tubes arranged in three rows, each having an internal diameter of **5** mm. Holes were drilled into the top plate of the box to admit the lower ends of the tubes, which were sealed in gas-tight with sealing wax. Asbestos paper was wrapped around the tubes **as** shown to prevent the infiltration of secondary **air;** they were also sealed with wax along the bottom and edges.

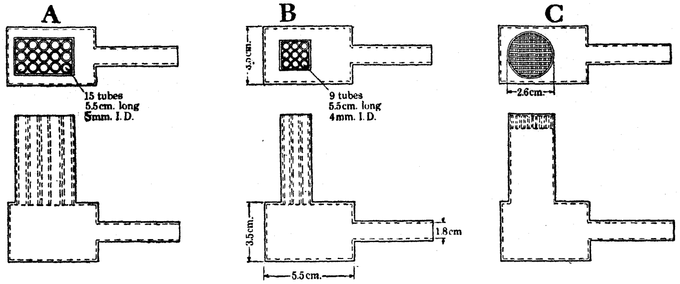

Fig. **2.—Gas** burners.

This burner could not be used with some of the unsaturated hydrocarbon gases, which have rather high flame speeds, due to the flames "flashing back" through the tubes. To handle these gases, type B was prepared similar to the foregoing with the exception that there were nine quartz tubes with an internal diameter of 4 mm. In some cases, even with this burner, it was very difficult to obtain satisfactory flames when the mixture contained oxygen in excess of that required for complete combustion. The flames tended to rise or "float" above the burners, or "flash-back" through the tubes.

Finally, a third burner of the Méker type was prepared. This was made as shown in *C*. The burner head was **2.6 cm.** in diameter and was provided with a nickel grid. Flash-backs were further prevented by installing 40-mesh nichrome screens both above and below the nickel grid when necessary.

Regulation of Flames.—The quantity of gas–air mixture was always regulated so that the inner cones remained close to the top of the burner ports. The quantity **was** then further regulated to give a rather bulky flame which spread out in cross-sectional area equal to the area of the burner ports. Consistent results were possible with any of the burners at a given gas–air ratio, provided that this condition obtained (see results shown in Fig. 4). If the flames tapered off toward the center as they left the burner ports, due to an insufficient amount of mixture being burned, low values were obtained. With some of the mixtures the metal Méker type burner tended to heat up slightly during use; therefore, it was necessary to surround the burner with a thick felt pad which was kept moistened with water. This does not seriously affect the temperature of the flame since any temperature lowering due to heating the burner is practically compensated by the increased temperature due to preheating the incoming gas, barring small losses by convection to the outside atmosphere.

Determination of Gas–Air Ratios.—The combustible gases were admitted to the apparatus either from a 12-cu. ft. gasholder or, in the case of the compressed gases, from tanks through a reducing valve. The quantity of gas admitted was determined by a calibrated flowmeter *j* (Fig. 1) from which the gas passed to the mixing chamber k. The air supply was forced through the apparatus by a Lehman rotary pump, having a by-pass arrangement whereby the air pressure could be maintained at any desired value. This regulation was obtained by a fine adjusting needle-valve. The air was then passed through three large stabilizing bottles, through the calibrated flowmeter *l*, a mercury pressure gage, a humidifier m, and thence through the atomizer in mixing chamber k, whence the gas–air mixture passed directly to the burner *c*. Samples of the gas–air mixtures were taken at *n* by mercury displacement. A small fraction of the sample collected was passed into a collecting tube, and the samples were analyzed in a Bone and Wheeler gas-analysis apparatus

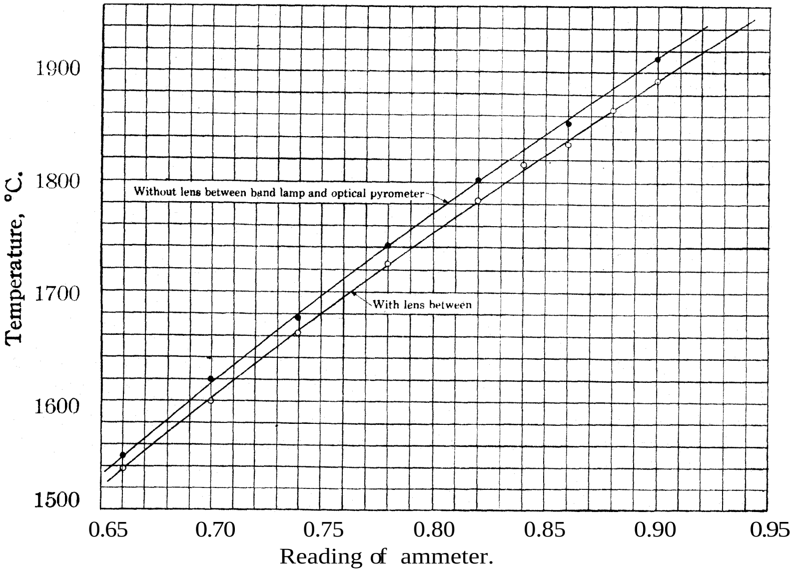

Fig. 3.—Calibration curve for tungsten band lamp and lens.

Calibration of Band Lamps.—General Electric 20-ampere type 4-T-20 tungsten band lamps were used as continuous radiators. Two different lamps were employed during the investigation. Experience with these band lamps showed that the brightness temperature for a given current consumption remained practically constant over long periods In the preliminary work the brightness temperature of the band lamp was read with an optical pyrometer each time an observation was made. However, by calibrating the band lamp with a calibrated optical pyrometer in which brightness temperature is plotted versus current, the time required to make observations was greatly reduced without sacrificing accuracy. The band lamps were calibrated by H. K. Griffin of the Physical Instruments Calibration Section of the Bureau of Mines and a typical calibration is given in Fig. 3.

Calibration of Lens Correction.—As the radiation from the Land lamp passes through a lens before being focused on the flame under investigation, a correction must be applied for the radiation absorbed by this lens. The correction is negative, because, with the

lens absorbing radiation, the lamp must be heated that much hotter before reversal takes place. The values for lens correction are given in Fig. 3. Over the range investigated it varies from 11 at 1600° to 21 at 1950°.

Color Correction.—Tests were made in which the flames were colored with sodium and lithium salts, supplemented by a few tests with thallium salts. As the brightness temperature of the band lamp is measured in the red (λ 0.665μ) and the temperature of the flame in the yellow (sodium salts, λ 0.589μ), red (lithium salts, λ 0.671μ) or green (thallium salts, λ 0.535μ) a color correction is necessary.

The correction for sodium is determined in the following manner. The relation between the true temperature T and the brightness temperature S_λ as derived from Wien's equation, is

$$\frac{1}{T} - \frac{1}{S_\lambda} = \frac{h2.303 \log ex}{C_2} \qquad (1)$$

and

$$\frac{1}{T} - \frac{1}{S_{\lambda'}} = \frac{\lambda' 2.303 \log e_{\lambda'}}{C_2} \qquad (2)$$

where T is black body temperature in absolute degrees; $\lambda = 0.665\mu$ (red light) or 0.0000665 cm.; $\lambda' = 0.589\mu$ (yellow light) or 0.0000589 cm.; e_λ and $e_{\lambda'}$ are spectral emissivities of red and yellow light; C_2 is 1.433 cm. degrees; S_λ is brightness temperature as observed with pyrometer; and $S_{\lambda'}$ is flame temperature (brightness temperature of yellow light). By subtracting Equation 2 from 1 we obtain

$$\frac{1}{S_{\lambda'}} = \frac{2.303}{C_2} [\lambda \log e_\lambda - \lambda' \log e_{\lambda'}] + \frac{1}{S_\lambda} \qquad (3)$$

Data for the spectral emissivities of tungsten as a function of the true and brightness temperature were obtained from Forsythe and Worthing.[12]

From the curves obtained by plotting μ against the spectral emissivity for different temperatures the spectral emissivity for any wave length can be read off for that temperature. Table I was constructed for the temperature range of these experiments.

TABLE I

SPECTRAL EMISSIVITIES FOR SEVERAL TEMPERATURES AT VARIOUS WAVE LENGTHS

True or black body temp., °K.	Brightness temp. in red, °K.	Spectral emissivity 0.665μ	0.589μ	0.671~	0.535μ
2100	1943	0.433	0.446	0.432	0.455
2200	2026	.431	.444	.430	.454
2400	2192	.427	.441	.426	.451
2500	2274	.425	.439	.424	.449

From Equation 3 at 1943°K. (in red), a corresponding temperature in the yellow is calculated. $S_{\lambda'}$ = 1965°K. or 22° higher in the yellow than

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[12] Forsythe and Worthing, Astrophys. J., 61, 146 (1925).

in the red. Table II contains the color corrections for sodium and lithium[13] over a range of temperatures.

TABLE II

COLOR CORRECTIONS

Temp., °K.	Sodium λ 0.589μ	Lithium λ 0.671μ
1943	+22	−2
2026	+23	−2
2192	+28	−2
2274	+30	−3

To check the accuracy of the calculated color corrections, saturated solutions of sodium and lithium nitrates were used in the atomizer. The flame temperatures were observed with ethane–air mixtures, the air–gas ratios being adjusted to give maximum values. Four different tests were made and the following results obtained.

TABLE III

COMPARISON OF SODIUM AND LITHIUM FOR OBTAINING TRUE FLAME TEMPERATURES

Test	Observed temperature, °C. Using sodium line	Observed temperature, °C. Using lithium line	True corrected flame temperature, °C. Sodium +26	True corrected flame temperature, °C. Lithium −2	Difference
1	1861	1888	1887	1886	− 1
2	1857	1893	1883	1891	+ 8
3	1870	1888	1896	1886	−10
4	1857	1878	1883	1876	− 7

In every case the observed temperatures for lithium salts are higher than those for sodium salts. When corrections are made for color, as previously described, the flame temperatures for both salts show fairly close agreement.

Introduction of Alkali Salts into Flame.—Both dry and wet methods were used to introduce sodium salts into the flames. In the dry method the air was passed through a quartz tube in which were placed three alundum boats containing the sodium salts. The quartz tube was heated in an electric furnace to a temperature sufficient to vaporize the sodium chloride in amounts which would produce a good reversal of the sodium lines in the spectrometer. The sodium chloride entered the burner in the form of a cloud. The air in these tests was not humidified before passing through the furnace, the moisture content being that of the laboratory air used. Considerable difficulty was experienced in maintaining a steady concentration of sodium in the flame, and it was necessary to cool the air back to

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[13] The reversal of the red lithium line was not as satisfactory as the sodium line. However, it could be employed by adjusting to the point of extinction. With the thallium line, however, it was impossible to obtain a reversal and the point of extinction was very indefinite. Flame temperatures obtained with thallium salts ranged from 100 to 140° below those obtained with sodium or lithium salts. The use of thallium salts is therefore impracticable.

room temperature by passing it through a lead coil immersed in cold water before mixing it with the combustible gas.

A wet method was finally adopted in which a saturated solution of sodium or lithium nitrate was placed in the atomizer chamber k and the salt solution atomized directly into the gas–air mixture. In the wet method the humidifier *m* was used to prevent the salt solution from crystallizing out on the nozzle of the atomizer and causing fluctuations in the rate of flow of air.

The cooling effect of the salt-solution spray was found experimentally by inserting a platinum strip in the non-luminous flame and reading its temperature with an optical pyrometer, with and without pure water being sprayed at the same rate as used in the measurements with the flames. The amount of cooling was found to be 15° for the hydrocarbon flames.[14]

A further series of tests was made with Pittsburgh natural gas–air mixtures in the ratios to give approximately maximum flame temperatures (1870 to 1890°) using both the wet and dry methods. In each case where the gas composition was the same the dry method gave higher results which varied over a rather wide range from 4 to 26°. These results appear to show that a correction for water spray is necessary. As an average value a plus correction of 15° has been added to all the results given in this report in which the wet method was used. The cooling effect of salt in the spray has been shown to be negligible.?

Gases.—Methane was obtained from a natural gas well near Pittsburgh, Pa. Previous tests of the gas from this well showed the combustibles to consist largely of methane. The gas from the well was compressed in steel cylinders by means of a portable compressor.

The natural gas was that supplied at the Pittsburgh Experiment Station, Bureau of Mines, and varies only slightly from day to day.

The ethane, propane, butane, isobutane, ethylene and butylene were all obtained from the Carbide and Chemicals Corporation of New York in steel tanks.

The propylene was obtained from the Ohio Chemical and Manufacturing Company of Cleveland, Ohio. This gas also was supplied in steel tanks.

A fractionation analysis of each of these gases was made at low temperatures and pressures, using a Shepherd and Porter apparatus for the fractionation and a Bone and Wheeler apparatus for the purity of the fraction. The results of these analyses are given in Table IV. All the gases indicate a small percentage of nitrogen. The high degrees of purity of the propane, butanes and butylene agree well with the specifications for these gases. Percentages less than 0.01% are not recorded. The usual combustion

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[14] The laboratory air was nearly always saturated with moisture so that the cooling effect observed is, in a large measure, due to droplets or a cloud of water picked up in the spray.

analyses in a gas-analysis apparatus give only the percentages of hydrocarbon gases in the gas–air mixtures on a dry basis, so that the percentages of gas given in the results described later are on a nitrogen and moisture-free basis.

TABLE IV

COMPOSITION OF GASES USED IN TESTS

Gas	Composition, per cent. by volume							
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4	C_3H_6	C_4H_8	N_2
Methane	97.8	1.4	0.1	0.1	..	..	..	0.6
Natural gas	86.6	7.9	2.7	1.3	..	..	..	1.5
Ethane	8.4	89.4	0.4	..	..	..	..	1.8
Propane	0.0	0.0	99.0	0.0	..	..	..	1.0
Butane	.0	.0	0.0	98.5	..	..	..	1.5
Isobutane	.0	.0	.0	99.5	..	..	..	0.5
Ethylene	1.0	1.5	.2	0.0	96.6	..	..	.7
Propylene	..	..	.5	..	3.5	93.3	1.1	1.6
Butylene	..	..	..	..	..	0.0	99.9	0.1

Experimental Results

The values found for the flame temperatures of methane, Pittsburgh natural gas, ethane, propane, butane, isobutane, ethylene, propylene and butylene when mixed with varying proportions of air are given in Fig. 4.

Vertical lines are drawn in the graphs representing the composition of the mixture to give complete combustion—that is, just sufficient combustible present to consume all the oxygen in the mixture. A shaded section is also drawn in each graph to show the range in percentage of combustible which has the maximum speed of uniform movement of flame. These values were taken from reports by Wheeler, Coward, Payman and others and represent the speed as measured in a 25-mm. tube for horizontal propagation of flame.

TABLE V

MAXIMUM FLAME TEMPERATURES OF HYDROCARBON GASES WHEN MIXED WITH AIR AND A COMPARISON OF THESE VALUES WITH THE MAXIMUM SPEED OF UNIFORM MOVEMENT OF FLAME

Hydrocarbon	Obs. max. flame temp., °C.	Combustible in air at maximum flame temp., %	Combustible in air necessary to give complete combustion, %	Max. speed of uniform movement of flame, cm./sec.	Combustible in air at max. speed of uniform movement of flame, %	Calcd. max. flame temp., °C.
Ethylene	1975	665–7.00	6.50	165	7.30–7.70	2072
Propylene	1935	4 45–4.90	4.45	100	5.00–5.40	2050
Butylene	1930	3.35–3.45	3.35	97	3.90–4.10	2033
Propane	1925	4.05–4.30	4.00	82	4.60–4.80	1967
Isobutane	1900	3.15–3.25	3.10	. .	.. ..	1973
Butane	1895	3.15–3.40	3.10	83	3.60–3.80	
Ethane	1895	5.70–5.95	5.65	86	6.30–6.60	1949
Pittsburgh natural gas	1890	8.60–9.10	8.60	71	9.10–9.40	1928
Methane	1880	9.45–10.10	9.45	67	9.70–10.00	1918

The variation in the flame temperature given represents the reproducibility that may be expected by this method. In obtaining these temperatures, four different investigators worked on the problem at one time or another, two different tungsten hand lamps were used, three different burners, both sodium and lithium salts, and both the wet and dry method of introducing the salts. The values found when using the different burners are properly noted in Fig. 4. They include corrections for water spray, color and lens, as given above. Table V contains a summary of results.

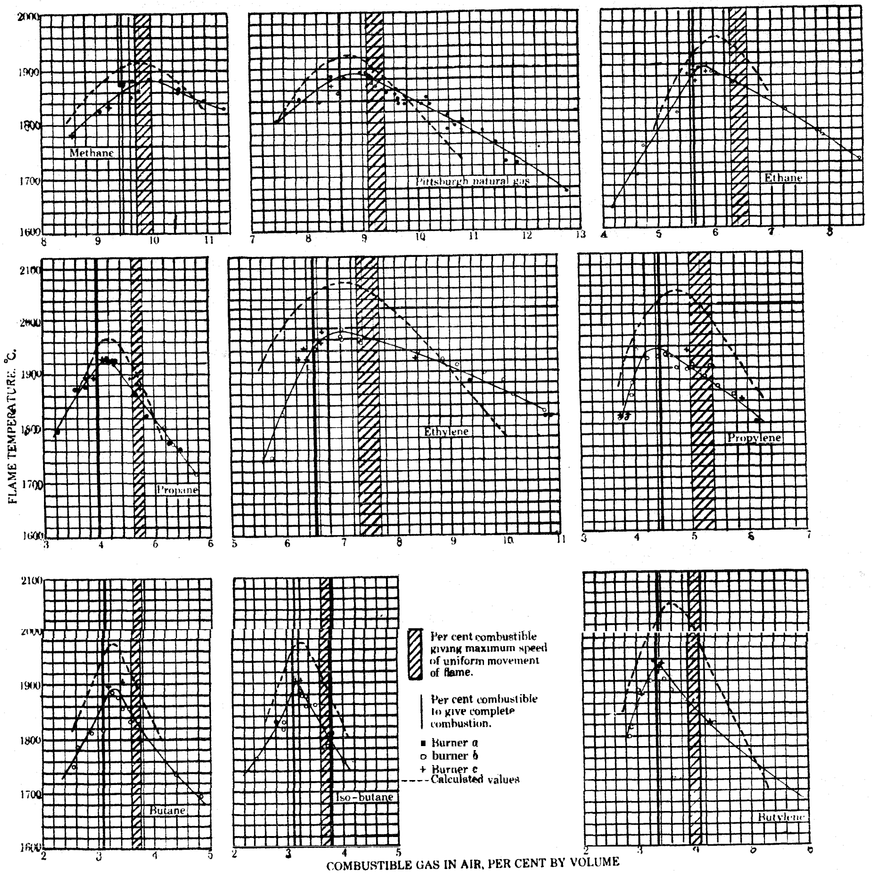

Fig. 4.—Flame temperatures of hydrocarbon gases.

Conclusions

The following conclusions may be drawn. 1. As would be anticipated, the flame temperature is markedly affected by the proportion of combustible gas in air. The flame temperature increases rapidly, starting with a mixture near the lower limit of inflammability and reaches a maximum when the mixture contains combustible slightly in excess of that necessary to consume all the oxygen present. The reason for this slight shift from a stoichiometric mixture lies in the dissociation of the products of combustion at the high temperatures developed. This is borne out by the calculated temperatures, whose maxima, allowing for dissociation, agree well with the observed maxima (refer to Fig. 4). With further increases in percentage of combustible the flame temperature falls again, although not as sharply as for the mixtures containing excess oxygen.

2. The maximum flame temperatures of the gases tested vary from 1880° for methane to 1975' for ethylene; the maximum variation among the different hydrocarbons is less than 100'.

3. The maximum flame temperatures of the unsaturated hydrocarbons are greater than those of the saturated hydrocarbons,

4. In most cases the maximum flame temperature occurs over a very narrow range of gas–air ratios; a slight change in the gas–air ratio at the maximum causes a sharp reduction in the flame temperature. This is especially true for propane, propylene, butane, isobutane and butylene and not so marked for methane, Pittsburgh natural gas, and ethylene.

5. The combustible gas–air mixture which gives the highest flame temperature does not correspond to that which gives the highest speed of uniform movement of flame, except for methane and possibly Pittsburgh natural gas. For all the other hydrocarbon gases the mixtures which give the highest flame temperatures contain less combustible gas than those which give the highest speed of flame.

6. There is a general agreement between the maximum flame temperatures and maximum flame speeds (Table V). Ethylene has the highest maximum speed of uniform movement of flame and also the highest flame temperature. The others are, on the whole, in the proper order in this respect. The variations as between propane, butane, and ethane are too small to draw significant conclusions. The reason for the non-coincidence of the mixtures which give maximum flame speeds and the maximum flame temperatures is not clear. It has been suggested that the maximum flame temperature may have little or nothing to do with the maximum flame speed but that some lower temperature at which the combustion reaches a certain rapidity may be of importance. In spite of the above-mentioned agreement this may well bear further investigation.

An explanation has been advanced by Payman and Wheeler[14a] to account for the disagreement between the maximum flame speed mixture and the stoichiometric mixture. According to them the displacement is due to a mass-action effect whose theoretical maximum occurs on the rich side. On the other hand, the highest calorific effect is produced by a stoichio-

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[14a] W. Payman and R. V. Wheeler, "Flame Speeds and Their Calculation," Reprinted from *Fuel* in *Science and Practice, 153 (1929).*

metric mixture. This factor will oppose the mass-action effect and will diminish the displacement of the maximum speed mixture caused by the latter. It is found that the temperature factor far outweighs the mass-action factor. The resultant displacement will be governed by the cooling effect of the excess combustible gas; the higher the specific heat of the latter at the temperature developed, the less the displacement will be. The displacement for propane and butane should therefore be less than for methane. Actually, it is slightly greater for propane, whereas for butane it is approximately the same as for methane. For ethylene, whose specific heat may also be expected to exceed that of methane, the displacement is twice as great.

Calculation of Flame Temperatures.—We have attempted to calculate the temperatures attained by the flame for the several mixtures used in this investigation. The agreements with the experimental flame temperatures are, in general, so satisfactory as to justify a brief account of these calculations.

In making the calculations the following assumptions have been made.

1. The initial mixture consists of hydrocarbon gas and air in any desired proportions.

2. The analyses given in Table IV are used for Pittsburgh natural gas and ethane. All other hydrocarbons are considered pure because the small amounts of impurities present introduce only very slight alterations in the final result.

3. The products of combustion consist of carbon dioxide, carbon monoxide, water, hydrogen, oxygen, nitrogen and no hydrocarbons.

4. The products of combustion are in chemical equilibrium at the temperature attained by the combustion. The equilibria considered are

$$\text{(a)}\quad 2H_2 + O_2 \rightleftharpoons 2H_2O$$
$$\text{(b)}\quad H_2 + CO_2 \rightleftharpoons CO + H_2O$$

5. The maximum temperature is reached when the products mixture attains the equilibrium condition. This assumption is not an unreasonable one when the combustion is very rapid.

6. The combustion takes place at constant pressure and one atmosphere.

7. The initial temperature $T_1 = 291°K.$, and the final temperature T_2 is the flame temperature sought.

8. The gases are saturated with water vapor at the temperature of the laboratory before being burned.

9. No heat is lost by radiation or conduction.

Method.—In general, the method employed is that used by Goodenough and Felbeck.[15] The following procedure was used.

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[15] G. A. Goodenough and G. T. Felbeck, *Bull. Univ. Ill. Eng. Exp. Station*, No. 139, March, 1924.

Initial mixture

1 $C_aH_{2b} = 1$ mole
2 $O_2 = c$ moles
3 $N_2 = d$ moles
4 $H_2O = e$ moles

Final mixture

1 $CO_2 = ax$ moles
2 $H_2O = (b + e)y$ moles
3 $CO = a(1 - x)$ moles
4 $H_2 = (b + e)(1 - y)$ moles
5 $O_2 = c + \frac{e}{2} - \frac{a}{2} - \frac{ax}{2} - (b + e)\frac{y}{2}$ moles
6 $N_2 = d$ moles

$$\text{Total moles} = m = b + c + d + \frac{a}{2} + \frac{3}{2}e - \frac{ax}{2} - (b + e)\frac{y}{2}$$

The number of moles of carbon, oxygen, and hydrogen should check in the initial and final mixture. x = fraction of carbon dioxide undissociated in the equilibrium mixture; y = fraction of water undissociated in the equilibrium mixture.

There are three unknowns—namely x, y, and T_2—and there must be three independent equations from which to determine them. Two are derived from the equilibria mentioned above and the third is obtained by applying the energy equation to the combustion process.

The equations expressing these equilibria are

$$K_{p\mathrm{H_2O}} = \frac{p_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}\sqrt{p_{\mathrm{O_2}}}} = \frac{y}{1 - y}\sqrt{\frac{m}{P\left(c + \frac{e}{2} - \frac{a}{2} - \frac{ax}{2} - (b + e)\frac{y}{2}\right)}}$$

Placing P = 1

$$\log K_{p_{\mathrm{H_2O}}} = {}^1/_2 \log m + \log \frac{Y}{1 - y} - {}^1/_2 \log \left(c + \frac{e}{2} - \frac{a}{2} - \frac{ax}{2} - (b + e)\frac{y}{2}\right) \quad (1)$$

$$K_{p_{\mathrm{wg}}} = \frac{P_{\mathrm{CO}}\, p_{\mathrm{H_2O}}}{p_{\mathrm{CO_2}}\, p_{\mathrm{H_2}}} = \frac{a(1 - x)(b + e)y}{ax(b + e)(1 - y)} = \frac{y(1 - x)}{x(1 - y)} \quad (2)$$

$K_{p_{\mathrm{H_2O}}}$ and $K_{p_{\mathrm{wg}}}$ are the equilibrium constants at constant pressure of the water formation and water-gas reactions.

In deriving the energy equation we apply the first law of thermodynamics and assume that no heat is lost in the combustion process. The following series of changes is assumed in passing from the initial to the final state. The mixture is completely burned at the constant initial temperature T_1; the products, carbon dioxide and water dissociate at the same T_1 until the composition of the mixture is the same as that in the final state of equilibrium; the final mixture at T_1 is heated without change of composition to the final temperature T_2.

The energy equation may be expressed as follows: heat of combustion of hydrocarbon = energy required to dissociate carbon dioxide and water + heat capacity of the final mixture from T_I to T_2. The final equation is

$$H_{\mathrm{HC}} = aH_{\mathrm{CO_2}} - axH_{\mathrm{CO_2}} + (b + e)H_{\mathrm{H_2O}} - (b + e)yH_{\mathrm{H_2O}} + ax\int_{291}^{T_2} C_{p_{\mathrm{CO_2}}}\,\mathrm{d}t$$

$$+ (b + e)\,y\int_{291}^{T_2} C_{p_{2\mathrm{HO}}}\,\mathrm{d}t + a(1 - x)\int_{291}^{T_2} C_{p_{\mathrm{CO}}}\,\mathrm{d}t +$$

$$(b + e)\,(1 - y)\int_{291}^{T_2} C_{p_{H_2}}\,dt + \left(c + \frac{e}{2} - \frac{a}{2} - \frac{ax}{2} - (b + e)\frac{y}{2}\right)\int_{291}^{T_2} C_{p_{O_2}}\,dt + d\int_{291}^{T_2} C_{p_{N_2}}\,dt$$

This can be represented by a linear equation of the type

$$Ax + By = C \tag{3}$$

where

$$A = a\left[\int_{291}^{T_2} C_{p(CO_2 - CO - 1/2\ O_2)}\,dt - H_{CO_2}\right]$$

$$B = (b + e)\left[\int_{291}^{T_2} C_{p(H_2O - H_2 - 1/2\ O_2)}\,dt - H_{H_2O}\right]$$

$$C = H_{HC} - aH_{CO_2} - (b + e)\,H_{H_2O} - \left(\frac{a}{2} + \frac{e}{2} + c + d\right)\int_{291}^{T_2} C_{p_{O_2\text{ or }N_2\text{ or }CO}}\,dt - (b + e)\int_{291}^{T_2} C_{p_{H_2}}\,dt.$$

H_{HC} = heat of combustion of hydrocarbon gas
H_{CO_2} = energy to dissociate one mole of CO_2 to CO and O_2
H_{H_2O} = energy to dissociate one mole of H_2O to H_2 and O_2

By eliminating y in (2) and (3) a quadratic equation in x is obtained

$$A\,(K_{wg} - 1)\,x^2 + x\,[(A + C) + (B - C)K_{wg}] - C = 0 \tag{4}$$

The procedure was modified slightly in the cases of Pittsburgh natural gas and ethane because these gases consisted of a mixture of hydrocarbons. In place of one mole of hydrocarbon a unit containing one mole of carbon was selected. The unit for Pittsburgh natural gas was therefore 1 mole of carbon, 1.85135 moles of hydrogen and 0.012965 mole of nitrogen: then $a = 1$, $b = 1.85135$, and the number of moles of nitrogen $= d + 0.012965$.

Choice of Data.—The heats of combustion of the hydrocarbons were calculated from data given in the "International Critical Tables."[16] The heats given below are in calories per gram mole of hydrocarbon gas forming carbon dioxide gas and water vapor at 18° and a constant pressure of one atmosphere.

TABLE VI

HEATS OF COMBUSTION OF GASEOUS HYDROCARBONS

Formula	Name	Calories per gram mole
CH_4	Methane	189,700
C_2H_4	Ethylene	310,885
C_2H_6	Ethane	336,732
C_3H_6	Propylene	458,532
C_3H_8	Propane	484,076
C_4H_8	Butylene	604,976
C_4H_{10}	Isobutane	630,620

H_{H_2O} at one atmosphere and 18° forming gaseous water = 57830 cal./mole, H_{CO_2} at one atmosphere and 18° = 67960 cal./mole.[17]

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[16] "International Critical Tables," Vol. V, 1929, pp. 138, 162.

[17] "International Critical Tables," Vol. V, 1929, pp. 176, 181.

The free energy data for the water–gas reaction were taken from Eastman.[18] The equilibrium constants at different temperatures were evaluated from the equation

$$\Delta F = 9800 - 3.06\, T \ln T + 7.912 \times 10^{-3}T^2 - 2.358 \times 10^{-6}T^3 + 3.258 \times 10^{-10}T^4 + I_6 T$$

where $I_6 = 5.60$.

The equilibrium constants for the formation of water were calculated from the expression given by Lewis and Friauf[19]—valid up to 2800°K.

$$\log K_{p_{H_2O}} = \frac{57296}{4.573T} - 0.848 \log T - 1.474 \times 10^{-4}T + 7.78 \times 10^{-8}T^2 - 8.72 \times 10^{-12}T^3 + 0.616$$

The specific heat equations for the various gases are

$$C_{p_{H_2O}}{}^{20} = 8.32 - 6.53 \times 10^{-4}T + 2.70 \times 10^{-6}T^2 - 6.145 \times 10^{-10}T^3$$
$$C_{p_{CO_2}}{}^{21} = 7.70 + 5.30 \times 10^{-3}T - 0.83 \times 10^{-6}T^2$$
$$C_{p_{H_2}}{}^{19} = 6.64 + 4.92 \times 10^{-4}T + 0.319 \times 10^{-6}T^2 - 0.74 \times 10^{-10}T^3$$
$$C_{p_{O_2, N_2, CO}}{}^{19} = 6.73 + 4.08 \times 10^{-4}\, T + 0.486 \times 10^{-6}T^2 - 0.1234 \times 10^{-9}T^3$$

Method.—Given a certain initial mixture of hydrocarbon gas, air and water vapor: a value for T_2 is assumed and A, B and C are evaluated. These are substituted in (4), which is solved for x; y is then obtained from (3). These values of x and y are substituted in the right-hand side of (1) and the value so found is compared with the true value of the equilibrium constant at the assumed temperature. If these do not agree, another temperature is assumed and the calculation repeated until they do agree. Both conditions of equilibrium and the energy equation are then satisfied. The amount of work may be materially lessened by constructing a plot of log $K_{p_{H_2O}}$ vs. T. The values for the right-hand side of (1) (from two temperatures assumed on either side of the true temperature) are entered on the plot. The line of intersection is the true temperature, provided that the two assumed temperatures are not too far removed from each other.

The results of the calculations are plotted as dotted curves in Fig. 4, on a moisture-free and nitrogen-free basis and are comparable with the experimental curves. The maximum temperature for each combustible is listed in the last column of Table V.

Discussion

The character of the agreement between the calculated and observed flame temperatures is evident from an inspection of Fig. 4. Of most significance is the position of the maximum temperatures. These occur

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[18] E. D. Eastman, "The Free Energy of Water, Carbon Monoxide, and Carbon Dioxide," U. S. Bureau of Mines Information Circular 6125, 1929, p. 7.

[19] Bernard Lewis and J. B. Friauf, THIS JOURNAL, 52, 3905 (1930).

[20] E. D. Eastman, unpublished report.

[21] E. D. Eastman, "Specific Heats of Gases at High Temperatures." U. S. Bureau of Mines Technical Paper 445, 1929, p. 27,

for mixtures slightly on the rich side, as is the case for the observed temperatures. The difference between calculated and observed temperatures is about 100° for the unsaturated and about 40 to 70° for the saturated hydrocarbons. As is to be expected, this difference is greater, in general, the higher the temperature. It should be noted that the calculated and observed curves cross each other in the region of rich mixtures. This is probably due to the infiltration of secondary air which, burning some of the excess hydrocarbon, gives rise to observed temperatures higher than would have been recorded were secondary air absent.

If we assume that the specific heat and free energy data are reasonably correct, the difference is due to radiation losses from the flames.

It is of interest to record that a similar set of calculations assuming the gas to be dry give temperatures 42 to 50° higher than for wet gases.

Acknowledgment.—The writers wish to thank J. S. Brown and H. Seaman, junior chemists, for their assistance in obtaining part of the experimental data and in making temperature calculations.

Summary

The flame temperatures for various hydrocarbon gas–air compositions have been measured for methane, Pittsburgh natural gas, ethane, propane, butane, isobutane, ethylene, propylene and butylene. The spectral-line reversal method was employed using sodium and lithium salt sprays. The flame temperatures reach a maximum when the mixture contains combustible slightly in excess of that necessary to consume all the oxygen present. These range from 1880° for methane to 1975° for ethylene. Comparison with the maximum speeds of uniform movement of flame shows that in general the latter is obtained for mixtures containing more combustible gas than those which give maximum flame temperatures. The flame temperatures of the various combustible gases have been calculated and the agreement is very satisfactory. The calculated maximum temperatures occur slightly on the rich side, as is the case for the observed values. These are higher than the observed values by about 100° for the unsaturated and 40 to 70° for the saturated hydrocarbons, and are in such a direction as to account for the difference by radiation losses from the flame.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 272]

THE POTENTIOMETRIC DETERMINATION OF IRIDIUM

BY SHO-CHOW WOO AND DON M. YOST

RECEIVED NOVEMBER 10, 1930 PUBLISHED MARCH 6, 1931

Introduction

In connection with a study of the reduction potential of the chloroiridous–iridic acids[1] it was necessary to develop good volumetric methods for the determination of the concentrations of the metal in its higher state of oxidation. In addition to this it was necessary to prepare solutions of chloroiridous and chloroiridic acids free from other elements of the platinum group and from the baser metals. Owing to the incomplete knowledge of the chemistry of the platinum group elements and the high cost of the iridium itself, both problems presented especial difficulties. In this paper are described a new method and a modified method for the volumetric determination of iridium, and incidentally the procedures used for the preparation of pure solutions of chloroiridous and chloroiridic acids.

The authors are indebted to Professor A. A. Noyes for valuable suggestions given during the course of the work.

Preparation of the Materials

Ammonium Hexachloroiridate.—Fairly pure metallic iridium in a finely divided state was first digested for three hours with a hot mixture of hydrochloric and nitric acids. This treatment removes any organic matter and the base metals as well as some of the platinum, the iridium not being much attacked. The residual metal was next intimately mixed with three times its weight of pure sodium chloride, and the mixture was heated to 650° for one hour in a quartz tube through which was passed a stream of chlorine. All of the platinum metals were converted by this procedure into the double chlorides. The mixture of the chlorides was dissolved in a small volume of dilute hydrochloric acid and the resulting solution was saturated with chlorine and then heated on a water-bath. This treatment resulted in the oxidation of the iridous to the iridic chloride and in the decomposition by heat of any quadrivalent palladium compounds.

To remove the palladium and rhodium, the solution of the chlorides was saturated with ammonium chloride and then cooled in an ice-bath. The precipitate (which contains the iridium) was filtered off and redissolved, and the solution was again precipitated as before. This procedure was repeated several times and yielded a product free from palladium and rhodium.

The resulting ammonium hexachloroiridate was next heated with concentrated nitric acid, fresh acid being added from time to time. To the residue in the flask was added concentrated perchloric acid, and the mixture was boiled until the greater part of the acid had been driven off; then more acid was added and the treatment repeated. Continued application of this procedure caused the complete volatilization of osmium and ruthenium as the tetroxides, leaving the iridium free from all platinum metals except platinum.

The residue was heated nearly to dryness and dissolved in a small amount of water

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[1] Sho-Chow Woo, THIS JOURNAL, **53**, 469 (1931).

To the solution was added an excess of sodium bicarbonate solution and bromine water, and the resulting mixture was boiled. This caused the precipitation of iridic hydroxide, but not that of platinum. The precipitate was redissolved in hydrochloric acid and subjected again to the bicarbonate precipitation. This tsratment was repeated several times. The final product, iridium hydroxide, was dissolved in hydrobromic acid and, after treatment with nitric and hydrochloric acids to convert the bromides to chlorides, the solution was saturated with ammonium chloride and cooled, and the resulting precipitate of ammonium hexachloroiridate was filtered off. In order to make sure that no sodium salts were present, the ammonium chloride precipitation was repeated several times The resulting ammonium chloroiridatc was washed with ice-cold water and then dried over concentrated sulfuric acid in a vacuum desiccator.

After each separation procedure a portion of the iridium-containing mixture was tested for the element being removed, using the dimethylglyoxime[e] test for palladium and the methods of Noyes and Bray[3] for the other elements. These tests show the presence of 0.3 mg. or less of the elements tested for. The procedures for the removal of osmium and ruthenium give a very complete separation, and the test for palladium is quite sensitive. Therefore the only contaminating elements present to the extent of 0.3% or less are rhodium and platinum, since the purification was always carried out until the tests for the contaminating elements were negative.

Chloroiridic and Chloroiridous Acids.—The ammonium chloroiridate was digested for ten hours with aqua regia upon a water-bath until all of the ammonia had been destroyed, and the nitric acid was then destroyed by repeated digestion with hot concentrated hydrochloric acid. The resulting solution consists principally of a mixture of chloroiridic acid and hydrochloric acid. For use in the electromotive force measurements a portion of this solution was reduced to chloroiridous acid with pure redistilled alcohol, using the procedure described by Delépine.[4] The small quantity of metallic iridium which separated was removed by filtering the solution through a hardened filter after the alcohol had been driven off by heating, and the solution was finally evaporated to dryness in a vacuum desiccator. The residue was dissolved in dilute hydrochloric acid of known strength.

Hydrochloric Acid **and** Other Analytical Reagents.—The best obtainable hydrochloric acid was redistilled and diluted with redistilled conductivity water. The other analytical reagents used were of C. P. grade.

The Methods of Analysis Studied

The iodometric method of analysis that has been described by Delépine[4] was first tested. In this method a hydrochloric acid solution of the chloroiridate is reduced to the chloroiridite by potassium iodide, and the liberated iodine is titrated with thiosulfate with starch as an indicator. In this form the method was not accurate since the color of the solution obscured the end-point; but it was found to give very satisfactory results when benzene was used to determine the point at which all of the iodine had been reduced. The titrations were carried out in 0.1 to 0.2 N hydrochloric acid solutions in a volumetric flask whose volume was such that the benzene layer rose

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[2] Wunder and Thuringer, *Z. anal. Chem.*, 52, 101–104, 660–664 (1913); H. B. Wellman, THIS JOURNAL, 52, 985 (1930).

[3] Noyes and Bray, "Qualitative Analysis for the Rare Elements," The Macmillan Co., Nrw York, 1929, pp. **39**, 117, 118.

[4] Delépine, *Ann. chim.*, **7**, 277 (1917)

into the neck when the last portions of thiosulfate were added. This procedure facilitated the determination of the end-point, especially when the narrow column of benzene was observed against a white background.

In the second method studied, titanous chloride was used for the estimation of quadrivalent iridium. This standardized reagent was added to a hydrochloric acid solution, and the end-point was determined electrometrically. During the initial stages of the titration the potential reaches a steady value after a short time, and at the end-point it changes abruptly from 0.65 to 0.4 volt. Some time, however, is required for the electromotive force to become constant near the end-point, and the stage at which the sharp change occurs may be considered to be the end-point only in case the titanous chloride is added very slowly. The addition of sodium chloride to solutions of chloroiridic acid free from other salts was found to increase the sharpness of the end-point. The initial concentration of the hydrochloric acid in the solutions titrated was from 0.1 to 0.2 N, and the total initial volume was 50 cc. The amounts of sodium chloride added to the titration mixtures varied from 2 to 3 g. The other half-cell consisted of a saturated calomel electrode.

For comparison the iridium in the ammonium salt and in the solutions was determined by the well-known gravimetric method of igniting the salt in a current of hydrogen. With the small amounts of material used extreme care was necessary to avoid the small accidental losses that usually accompany this method of analysis. The determinations differed by less than 1% in all cases, usually by not more than 0.5%.

An attempt was also made to determine iridium by precipitating it with strychnine sulfate, but the precipitation was found to be incomplete.

Results of the Test Analyses

In Tables I, II and III are presented, the results of analytical experiments in which the above-described methods were used. The iridium solutions were measured by weighing them in a pipet designed for the

TABLE I

CONSISTENCY OF THE RESULTS BY THE IODOMETRIC METHOD AND COMPARISON WITH THOSE BY THE TITANOUS CHLORIDE TITRATION

No.	H_2IrCl_6 soln., g.	Solution used, cc. $Na_2S_2O_3$	Solution used, cc. $TiCl_3$	Iridium per gram of solution. mg.
1	2.0483	7.57	..	4.44
2	3.2762	12.10	..	4.44
3	2.5943	9.56	..	4.43
4	10.3615	14.05	..	1.630
5	10.4763	14.23	..	1.634
6	8.1114	11.00	..	1.630
7	9.4657	...	8.03	1.629
8	10.4119	...	8.87	1.635
9	11.2136	...	9.55	1.634

TABLE II

COMPARISON OF THE IODOMETRIC AND GRAVIMETRIC METHODS

Expt.	Milligrams taken $(NH_4)_2IrCl_6$	 Iridium	Milligrams of iridium found Iodometric	 Gravimetric
1	37.4	16.3	16.3	..
2	47.5	20.8	20.7	..
3	68.3	29.8	29.7	..
4	68.3	29.8	29.8	..
5	81.3	35.5	..	35.6

TABLE III

IODOMETRIC, TITANOMETRIC AND GRAVIMETRIC RESULTS COMPARED WITH THE CALCULATED IRIDIUM CONTENT OF AMMONIUM CHLOROIRIDATE

Method	$(NH_4)_2IrCl_6$ soln., g.	Milligrams of iridium per gram of solution Found	 Present[a]
Iodometric	7.3742	2.758	
Iodometric	6.8145	2.763	
		Mean 2.761	2.766
Titanous chloride	9.6965	2.755	
Titanous chloride	8.7137	2.755	
Titanous chloride	9.0680	2.755	
		Mean 2.755	2.760
Gravimetric	15.9696	2.786	
	15.3795	2.766	
		Mean 2.776	2.766

[a] As calculated from the amount of $(NH_4)_2IrCl_6$ known to be present per gram of solution.

purpose. The thiosulfate used was 0.00623 N. The titanous chloride used was 0.00994 N for the experiments of Table I and 0.009285 *N* for those of Table III.

It is seen from the tables that the two volumetric methods yield concordant results, the maximum deviation from the mean being about 0.3%. Moreover, the amount of iridium in the salt $(NH_4)_2IrCl_6$ as determined volumetrically and gravimetrically is, within a few tenths of one per cent., the same as that calculated from the formula."

Summary

The results (given in Tables I–III) show that the new titanometric method of determining iridium gives results in agreement with those given by the earlier iodometric method, which was refined by using benzene to

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[5] This tendency to form non-hydrated chloro salts is not found with some other platinum metals. The results of Howe [THIS JOURNAL, 49, 2381 (1927)] and of Crowell and Yost [*ibid.*, 50, 374 (1928)] emphasized this for the case of ruthenium, and at the same time clarified an important question in the chemistry of coordination compounds. Werner, "Neuere Anschaungen auf dem Gebiete der anorganischen Chemie," Vieweg und Sohn, Braunschweig, 1909, 2d. ed., p. 292.

detect the liberated iodine. Both these methods gave results in agreement with the gravimetrically determined amounts of iridium present in the solutions. They show, moreover, that the iridium content of crystalline ammonium hexachloroiridate as determined volumetrically and gravimetrically is the same, within a fraction of one per cent., as that calculated from the formula $(NH_4)_2IrCl_6$.

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[CONTRIBUTION NO. 649 OF THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

ACIDITY IN NON-AQUEOUS SOLVENTS. CONDUGTIMETRIC AND ELECTROMETRIC TITRATIONS OF ACIDS AND BASES IN BENZENE

BY VICTOR K. LA MER AND HAROLD C. DOWNES

RECEIVED NOVEMBER 14, 1930 PUBLISHED MARCH 6, 1931

I. Introduction

When we consider the remarkable successes which the theory of Arrhenius achieved in correlating such diverse properties of aqueous solutions as (a) conductivity, (b) osmotic properties, (c) acid and base catalysis, (d) hydrogen electrode potentials, and (e) indicator effects, it is quite natural that the degree of acidity should have been taken as synonymous with the concentration of hydrogen ions behaving osmotically as solute particles independent of the acid ionogen. In other words, it has been tacitly assumed that on passing from one solvent to another the purely thermodynamic properties like (b) and (d) will run parallel to properties like (a) and (c) which depend only indirectly upon thermodynamic relations. On this view the acidity of an acid dissolved in benzene should at best be very small, since its degree of dissociation as judged by conductivity is very minute.

The experimental work of Hantzsch,[1] of Brönsted,[2] and of Hall and Conant,[3] is primarily responsible for demonstrating that this assumed

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[1] (a) Hantzsch, Z. *Electrochem.*, 29, 230 (1923). Hammett, THIS JOURNAL, 50, 2666 (1928), gives complete references of Hantzsch's work up to 1928 and presents the salient features. Later papers of importance are (b) Hantzsch and Voigt, *Ber.*, 62,975 (1929); (c) Hantzsch and Buroway, ibid., 63, 1180 (1930).

[2] Brönsted, (a) Z. *physik. Chem.*, *108*, 217 (1924), with Kai Pedersen, (b) *Rec. trav. chim.*, 42, 718 (1923) (definition of acids and bases). Similar views were presented independently by Lowry, *Trans. Faraday Soc.*, 20, 58 (1924); *Chemistry Industry*, 42, 43 (1923); (c) J. *Phys. Chem.*, 30,777 (1926); (d) THIS JOURNAL, 49, 2554 (1927), with E. A. Guggenheim (catalysis by undissociated molecules); (e) *Ber.*, 61 2049 (1928) (indicators in benzene); (f) Z. *physik. Chem.*, 143, 301 (1929) (acidity and ion potentials); (g) *Chem. Rev.*, 5, 284 (1928) (review of subject).

[3] (a) Hall and Conant, THIS JOURNAL, 49,3047,3062 (1927); (b) Hall and Werner, *ibid.*, 50, 2367 (1928); (c) Hall, J. *Chem. Ed.*, *7*, 782 (1930); (d) THIS JOURNAL, **52**, 5115 (1930).

parallelism between thermodynamic and non-thennodynamic properties does not hold. The lines of evidence which they have adduced in support of the view that the classical consideration of acids and bases must be modified if it is to apply to non-aqueous solvents and even certain properties of aqueous solutions as (2) below, are: (1) properly chosen indicators respond promptly to additions of acids and bases when dissolved in solvents like glacial acetic acid[3a,4] or benzene,[2e,1b] whereas the conductivity indicates extremely low ionization; (2) acid (or basic[2"]) catalysis is produced by undissociated acids[Zd] (or bases), the catalysis being dependent primarily upon the facility with which protons can be transferred from catalyst to substrate (or *vice versa);* **(3)** the degree of dissociation[2b,2c] as indicated by the conductance ratio in any given solvent depends not only upon the dielectric constant but also upon the extent of combination of the acid with the solvent acting as a base, yielding a highly dissociated electrolyte popularly called a salt.

As far as we are aware, the possibility of titrating acids and bases electrometrically in solvents like benzene whose role is that of an inert diluent has never been considered. It is obvious if an electrometric titration can be carried out that an important experimental method becomes available since electrometric titration presents in simplest form the essential features of the capacity and intensity factors of acidity.

II. Experimental

A. Conductimetric **Titrations.**—Walden and Gloy[5] have demonstrated that certain salts like the tetra isoamyl ammonium halides, perchlorates, thiocyanates and picrates, (R_4NX), are appreciably soluble (iodide about 0.1 *m* at 72°) in benzene and conduct the current. No corresponding work has been reported for acids and bases.

In order to explore to what extent salt formation may proceed in benzene, we determined the changes in conductivity produced on alternate additions of acids and bases. A very low resistance cell consisting of two platinum electrodes having an area of about 8 sq. cm. held rigidly about 2 mm. apart by glass supports contained the solutions studied. The resistance was measured by noting the deflections on a Leeds and Northrup galvanometer, type 2500, when the cell and galvanometer were placed in series with the 110-volt direct current line. By shunting a variable resistance across the galvanometer, the range of measurement can be greatly extended. Cady and Lichtenwalter,[6] using this method, noted that polarization effects of a few tenths of a volt were present. In our work all

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[4] Nicholas Dietz, Dissertation, Columbia University, 1930 (formic acid as solvent); Hammett and Dietz, THIS JOURNAL, 52, 4795 (1930).

[5] Paul Walden, "Acids, Bases and Salts," McGraw-Hill Book Company, Inc., New York, **1929.** Gloy, Dissertation, Rostock, **1927;** Chem. Abst., **23,** 5088 (1929).

[6] Cady and Lichtenwalter, THIS JOURNAL, 35, 1434 (1913).

readings were checked by reversing the direction of the current through the cell. We found that the deflections in either direction were sensibly identical and reproducible within the accuracy of the measurement.

In one typical run we employed 1.11 M trichloroacetic acid and 0.834 M diethylamine as the acid and base. The results are plotted in Fig. 1: the ordinates are in reciprocal ohms times 10^{11} and the abscissas in cc. of added base or acid calculated to molar values. The solid dots represent a repetition of the experiment and give a measure of the reproducibility. The arrows indicate the equivalence points where stoichiometrically equal quantities of acid and base were present. The conductivity appears to be unchanged on addition of trichloroacetic acid to benzene, at least up to 0.04 M. At that point diethylamine was added; the conductivity rose sharply, reaching a maximum and then decreasing to a value very little greater than that for benzene, when the equivalence point was reached. The equivalence point in the titration corresponds closely with a region of minimum conductivity.

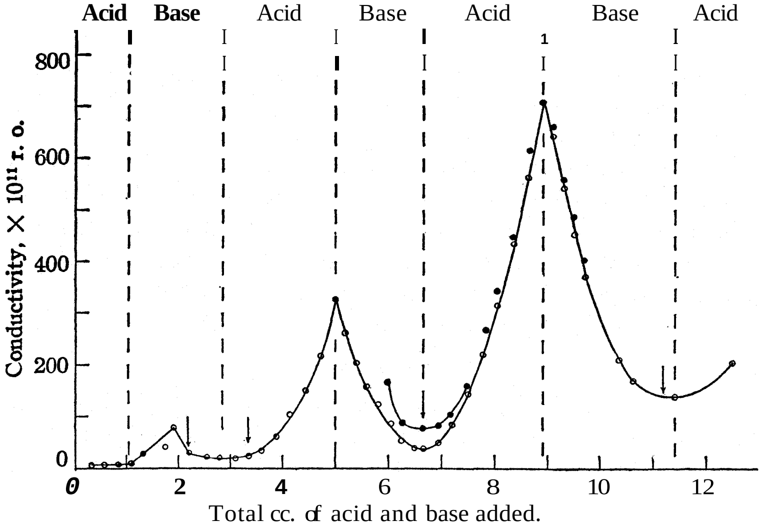

Fig. 1.—**Conductimetric titration** of diethylamine by trichloroacetic acid.

In another run (not shown) where diethylamine was first added to benzene, the conductivity remained sensibly constant (80 X 10^{-11} r. o.) up to about 0.05 M, when it rose sharply to a maximum at about 0.06 M, then decreased to a value which remained constant on addition of trichloroacetic acid until the equivalence point was passed. Further additions of acid then produced relatively rapid increases in conductivity, reaching a value of 1290 × 10^{-11} r. o. for a solution containing 0.220 M acid and 0.08 M base.

Paul Walden[7] states that *"the equivalent conductivity in benzene decreases with increasing dilution."* A plausible explanation for these curious anomalies has been presented by Gross and Halpern[8] in a paper which has received scant attention to date. Their argument may be stated as follows. The addition of an electrolyte like potassium nitrate increases the dissociation of a weak acid like acetic acid in water, by reducing the activity coefficients of the hydrogen and acetate ions by the now well-established mechanism of interionic attraction. In a low dielectric solvent like benzene the dissociation of acids is extremely minute but nevertheless exists, as demonstrated by our own conductivity measurements.

When the electrolyte concentration is increased either by adding excess acid or better by adding base leading to salt formation, the values of the activity coefficients of the dissociated ions of the acids are reduced more than the corresponding conductivity coefficients. Increased equivalent conductance should therefore result.

The Debye–Hückel limiting law predicts that the value $-\log f$ should increase at a rate $(78/2.29)^{3/2} = 200$ times greater in benzene than in water; *i. e.*, the logarithm of the stoichiometric equilibrium constant would be increased 200 times more in benzene than in water at the same ionic strength.

The complete solution of the Poisson–Boltzmann equation given by Gronwall, La Mer and Sandved[9] show, contrary to the case in water, that in a solvent of low dielectric constant the terms of higher order than the first are of sufficient magnitude in the case of uni-univalent salts to completely overwhelm and change the sign of the contribution for ion size yielded by the Debye first approximation since D appears in the denominator to progressively higher powers for each order of approximation.[10] The relative increase in equilibrium constant in benzene as compared to water must be very much greater than any prediction based on the limiting law alone. The general solution consequently strengthens the proposal advanced by Gross and Halpern.

B. Electrometric **Titrations.**—The cell consisted of a Jena glass

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[7] Ref. 5, p. 266.

[8] Gross and Halpern, *Physik. Z.*, 26, 636 (1925).

[9] Gronwall, La Mer and Sandved, *ibid.*, 29, 358 (1928).

[10] Detailed computations by V. K. La Mer on the magnitudes of the contributions of the higher terms and their ability to account for the striking data of Kraus and Seward for the solubility of sodium chloride in isopropyl alcohol D = 16 and the data of A. L. Robinson for various salts in acetone D = 21.3 were presented at the Columbus (April, 1929) Meeting of the American Chemical Society (see V. K. La Mer, "Annual Survey of American Chemistry, 1928–1929," 1930, Vol. IV, p. 12). Bjerrum's hypothesis of ion association yields the same qualitative result but at the expense of an additional and unnecessary hypothesis. For more recent data on solubility in ethyl alcohol, see Seward and Schumb, THIS JOURNAL, 52, 3962 (1930).

crucible with a porous bottom of sintered glass rested in a small beaker. The electrodes were of platinum and placed close to both sides of the glass diaphragm. Even after saturating the benzene with tetra isoamyl ammonium iodide, the resistance of the cell is far too high for the sensitivity of the ordinary galvanometer. The method of discharging a condenser through a ballistic galvanometer as described by Beans and Walden[11] is admirably suited for the purpose. We have found that potential differences could be measured to ±0.1 mv. with a 10 microfarad condenser, using the apparatus as a null point instrument. This procedure does not require the complete charging of the condenser and is almost as rapid as the method using the type 2500 galvanometer. Thiophene-free benzene was employed without any special effort to dry it completely since exposure to air could not be eliminated with a cell of this construction.

A typical cell may be represented as

Pt	Trichloroacetic acid (0.165 m) diethylamine (0.0413 m) tetra isoamyl ammonium iodide (satd.) quinhydrone (a)	trichloroacetic acid (0.165 m) diethylamine (x) tetra isoamyl ammonium iodide (satd.) quinhydrone (a)	Pt

where x is initially 0.0413 M but is increased by addition of base in the course of the experiment; (a) is undetermined but constant. The cell was assembled by saturating a quantity of benzene with tetra isoamyl ammonium iodide, then adding quinhydrone. A measured amount of this solution was put into the beaker and the desired amount of acid–base mixture (2 to 1 ratio of acid to base) added to it. A known aliquot was then pipetted into the crucible compartment which served as the titration vessel.

The saturating salt was washed with ether and recrystallized from benzene. The acid and base solutions were made up in benzene, roughly 1.0 molar and standardized against aqueous sodium hydroxide and hydrochloric acid with continuous shaking until the indicator change occurred in the water layer. The titrating solutions in this experiment were trichloroacetic acid, 1.111 ± 0.002 molar and diethylamine, 0.834 ± 0.001 molar.

Unless the initial potential was zero to within 3 mv., the electrodes were cleaned and the cell reassembled. Diethylamine was then added (about 1.2 milliequivalents at a time) and the potential measured after each addition until a large increase in potential, followed by a relatively slow increase, was observed. In some cases additions of trichloroacetic acid were made to the solution containing excess base. The potential returned to a value approximating the initial one. When the solution was strongly basic the color changed rapidly from pale yellow to red which we attribute

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[11] H. T. Beans and George Walden, THIS JOURNAL, 50, 2673 (1928); George Walden, Dissertation, Columbia University, 1924,

to reaction with the quinhydrone. It was for this reason that we made up the standard solution by adding a 2 to 1 mixture of trichloroacetic acid and diethylamine rather than adding the pure components. A small amount of iodine dissolved in benzene gave a strong test for iodine with starch, but since the red solution gave no test with starch we could not attribute the color to iodine formed by reaction of the quinhydrone with the iodide. In strongly acid solution the same color change was observed, although it did not proceed as rapidly.

The reaction may be formulated[12] as follows

$$\mathrm{HA} + \mathrm{R_2NH} \rightleftharpoons \mathrm{R_2NH_2^+} + \mathrm{A^-} \tag{1}$$

where HA is trichloroacetic acid and R_2NH is diethylamine. For the quinhydrone electrode where $C_{\text{quinone}} = C_{\text{hydroquinone}}$

$$E = E_0' + RT/NF \ln a_{\mathrm{H^+}} \tag{2}$$

The activity coefficients of quinone and hydroquinone are assumed to be constant during the titration and included in E_0'. The presence of the tetra isoamyl ammonium iodide instead of complicating actually simplifies the theoretical interpretation of the cell since its presence stabilizes the activity coefficients during the progress of the titration by maintaining a more nearly constant environment, and by eliminating junction potential Abundant proof[13] now exists that the addition of an excess of a foreign neutral salt is the simplest way of eliminating these difficulties in aqueous solution, and the same principle should obtain in benzene. Owing to the much greater interionic effects in benzene it is important to reduce these disturbances as far as possible.

When trichloroacetic acid is in excess, the hydrogen-ion activity is most conveniently formulated in terms of its dissociation, hence[14]

$$a_{\mathrm{H^+}} = Ka_{\mathrm{HA}}/a_{\mathrm{A^-}} \tag{3}$$

or

$$E = E_0 + RT/NF \ln a_{\mathrm{HA}}/a_{\mathrm{A^-}} \tag{4}$$

where

$$E_0 = E_0' + RT/NF \ln K \tag{5}$$

Since we have no means of determining the absolute value of E_0' we have arbitrarily taken the potential of the reference electrode (2 trichloroacetic acid : 1 diethylamine) as zero, and plot only the differences in electromotive force as the titration proceeds. The further addition of base (diethylamine) by definition reduces the escaping tendency of protons (hydrogen

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[12] Although the product is written in ionic form, the number of free ions in benzene solution is extremely small owing to the low dielectric constant.

[12] La Mer and Sandved, THIS JOURNAL, **50**, 2656 *(1928)*. References to earlier work are given on page 2658.

[14] Regarding formulation see W. Mansfield Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Maryland, Chap. XXVII, particularly p. 529. Also Brönsted, Ref. 2 g, pp. *238*, 289.

electrode potential) by the process represented by (1). As Fig. **2** shows, the proton potential curve on changing the relative amounts of acids and bases shows a close analogy to the neutralization curves of these acids and bases as ordinarily formulated for aqueous solution. When an amount of diethylamine greater than the stoichiometric equivalent, which is represented by the upturned arrow in Figs. **2** and **3**, has been added, we pass to a new level of acidity which is determined by the ratio of $R_2NH_2^+$ to R_2NH°. The potential is then given by

$$E = E_0'' + RT/NF \ln (R_2NH_2^+)/(R_2NH^\circ)$$

The most convenient means of characterizing the relative acidities (proton escaping tendencies) of the two conjugated systems (HAc°/Ac^-) and $(R_2NH_2^+)/(R_2NH^\circ)$ are by the values of E_0' and E_0'', respectively, which are equal to the respective values of E when the ratio is unity or the systems are at the half neutralization points. Our data are hardly sufficiently accurate or extensive to test the shape of the curves by plotting E against log $(R_2NH_2^+)/(R_2NH^\circ)$ or log (HA°/A^-), but there can be little doubt but that the proton potential of the system diethyl ammonium $\rightleftarrows$ diethylamine is 0.40 volt less than for the system trichloroacetic acid $\rightleftarrows$ trichloroacetate.

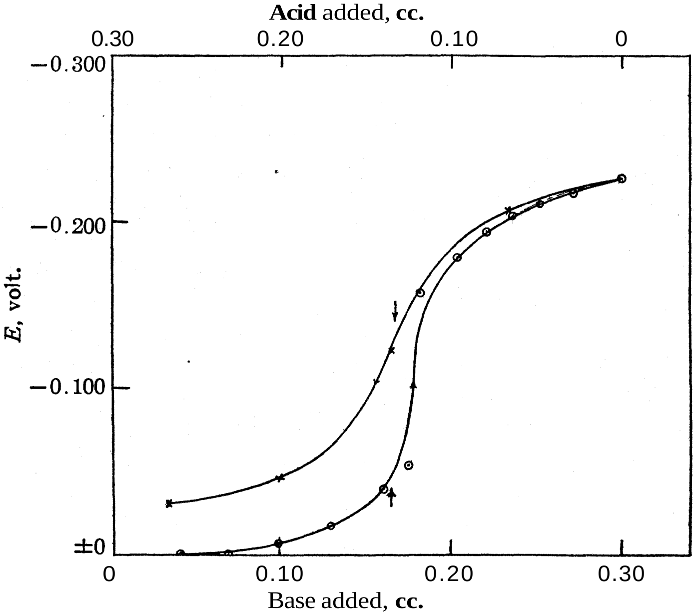

Fig. 2.—Electrometric titration of diethylamine–trichloroacetic acid.

As a test upon the reversibility of the process we added trichloroacetic acid to the solution containing excess base, as shown by the upper curve in

Fig. 1. The curve for this back titration does not correspond exactly to the forward curve. This may be due to possible diffusion through the porous glass membrane or to changing environmental effects during the titration. More work must be undertaken before this point can be regarded as settled. The fact that the equivalence point (downward arrow of Fig. 2) coincides as closely as it does with the point of inflection is strong evidence that acid–base relations in benzene are quite analogous to those in water as far as potential is concerned.

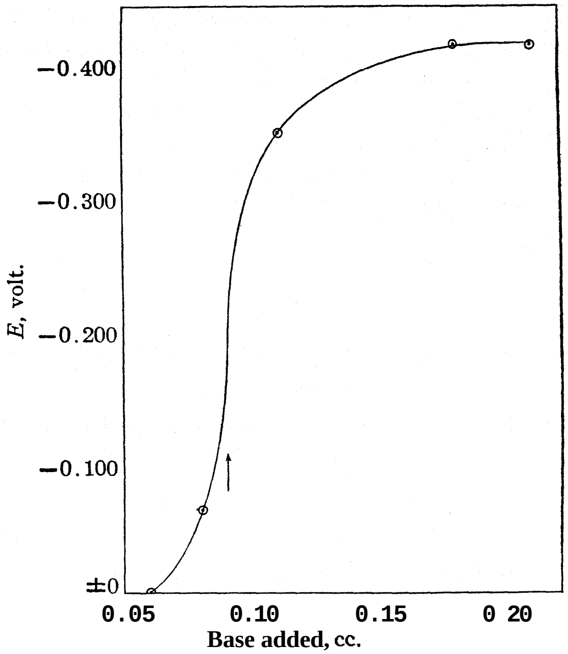

Fig. 3.—Titration of 3 cc. of (0.0266 *M*) trichloroacetic acid in benzene by diethylamine (1 M) in benzene. Equivalent point, 0.08 cc.

The question arises, would these curves be obtained in absolutely dry benzene?" The saturation value for water in benzene is given as 0.57 part per thousand at 20°. It hardly seems likely that the still smaller amount of water in equilibrium with the atmosphere could be entirely responsible for the conductivity and electrometric titration curves. However, we must point out that although indicator changes are immediate and reproducible in moist benzene, one of us (V. K. L.) has observed that this does not always hold true when benzene is dried over sodium. We prefer to leave open the question of the effect of traces of water until a more refined technique has been developed.

[15] E. Juanita Greer, This Journal, 52, 4191(1930).

We wish to thank Dr. George Walden for placing his electrical instruments at our disposal.

III. Summary and Conclusions

1. An electrometric method is described for titrating acids and bases in benzene using quinhydrone electrodes.

2. The curve obtained when trichloroacetic acid is titrated electrometrically with diethylamine has the same characteristics that are observed in aqueous solution on titrating a strong acid with a strong base.

3. The difference in hydrogen electrode potential (proton escaping tendency) between the trichloroacetic acid system and the diethylammonium acid system is of the order of 400 millivolts.

4. Conductivity titrations of acids and bases in benzene exhibit the anomalous behavior similar to that reported by Paul Walden for salts in benzene. The equivalence points correspond to minima regions in the conductance titration curves.

New York, N. Y.

[Contribution from the Chemical Laboratory of the University of California]

REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION.

III. THE REDUCTION OF IODATE ION BY HYDROGEN PEROXIDE[1]

By Herman A. Liebhafsky

Received November 29, 1930 Published March 6, 1931

The equations and the free energy data[2] for the reactions

$$2IO_3^- + 2H^+ + 5H_2O_2\,(aq) = I_2(s) + 6H_2O + 5O_2;\ \Delta F^\circ - 118.850\ \text{cal.} \qquad (1)$$
$$I_2(s) + 5H_2O_2(aq) = 2IO_3^- + 2H^+ + 4H_2O;\ AF^\circ = -132{,}050\ \text{cal.} \qquad (2)$$

make it evident that the I_2–IO_3^- couple is capable of catalytically decomposing hydrogen peroxide. The present investigation was begun with an extensive series of experiments on the iodine–iodate catalysis, but the results obtained proved to be so complex that no definite conclusions concerning the mechanism of the catalysis could be drawn from them alone. These data showed, however, that the catalysis was the result of several compensating reactions, of which two--the oxidation of iodine by hydrogen peroxide and the reduction of iodate ion by that same substance—gave hope of being suitable for separate study. In the second paper of this series there have been presented some experimental results on the former

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[1] The preceding papers of this series are Part I, Bray and Liebhafsky, This Journal, **53, 38** (1931), and Part II, Bray and Caulkins, *ibid.*, **53**, **44** (1931).

[2] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp 607–608.

reaction (Equation 2). To determine, in so far as is possible by chemical and kinetic methods, the character of the steps underlying the reduction of iodate ion by hydrogen peroxide (Equation 1) is the purpose of this paper.

A reaction system corresponding entirely to the "pure" reduction of iodate ion according to Equation 1 has never been experimentally realized. When peroxide and iodate are mixed in acid solution, the initial formation of a small amount of iodine is followed by the establishment of a "steady state" in which the main reaction is the catalytic decomposition of hydrogen peroxide (cf. Part I). The amount of such catalysis is a complicated function of the concentration of iodine in the system; it seemed almost certain, that by maintaining this iodine concentration as low as possible, the rates of the reactions resulting in catalysis could be reduced. The minimizing of the amount of this catalysis is the first requirement which any experimental method for the study of the reduction of iodate ion must fulfil.

An effective means for meeting this requirement is provided by placing the reaction mixture in contact with carbon tetrachloride and shaking the whole at a rate sufficient to insure rapid extraction of the iodine. Part of the carbon tetrachloride can be withdrawn and replaced immediately by an equal volume of fresh solvent at convenient time intervals; the rate of formation of iodine may be followed by titrating the samples withdrawn. That dI_2/dt thus determined can measure accurately the rate of reduction of iodate ion by hydrogen peroxide will be shown in a later section. Since small amounts of iodine can be determined with relatively high accuracy, and since the reaction is not extremely rapid at the temperatures employed, an accurate value of dI_2/dt can be obtained before the concentration of any of the reacting substances has changed enough to affect this rate beyond the experimental error. The order of the reaction with respect to any substance may be obtained, therefore, from a series of measurements in which only the concentration of that substance is varied.

Experimental Part

C. P. reagents not further purified were used. Permanganate solution standardized against sodium oxalate served for the analysis of peroxide solution, and for the standardization of the thiosulfate solution used in all iodimetric work. The potassium iodate solution was analyzed iodimetrically. Perchloric acid standardized against sodium carbonate was used as the source of hydrogen ion.

Two-hundred cc. glass flasks with conical bottoms were used as reaction vessels; to the acid iodate solution in these flasks 25 cc. of carbon tetrachloride was added, and the whole shaken in an oil thermostat in a dark room at the rate of 120–130 double shakings a minute The hydrogen peroxide was added from a reservoir in the thermostat with a pipet after the attainment of temperature equilibrium; the initial time was taken as that at which the pipet was half emptied; 20-cc samples of the carbon tetrachloride in the reaction mixture were withdrawn as follows The shaker was stopped at a time taken as the time of the sample. After a twenty-second interval,[3] allowed to insure a complete separation of the two layers, the sample was pipetted into a glass-stoppered flask containing water which served both to wash the carbon tetrachloride and to prevent its loss by volatilization. After two further washings in a separatory funnel, the carbon tetrachloride containing the iodine was transferred into a flask containing weakly acid potassium iodide solution, and then titrated with thiosulfate solution of convenient concentration; the most dilute solution of sodium thiosulfate practicable was found to be 0.002 N. For purposes of calculation, all results were expressed in terms of 0.1 N sodium thiosulfate. Experiments in dilute solutions depended upon the titration of amounts of iodine equivalent sometimes to 0.01–0.02 cc. of 0.1 *N* thiosulfate. These titrations were carried out according to a method previously outlined.[4]

Measurements of dO_2/dt were carried out in the usual manner with the aid of gas burets; the time intervals for the readings were so chosen that the presence of the carbon tetrachloride had no disturbing effect due either to the establishment of the equilibrium vapor pressure of carbon tetrachloride, or to the saturation of the carbon tetrachloride with oxygen. The same dO_2/dt was obtained initially from experiments of the same composition when the one reaction mixture was in contact with carbon tetrachloride while the other was not. Since such agreement was obtained repeatedly without considering the vapor pressure of carbon tetrachloride in calculating the volume of oxygen evolved in the first case, all later results were calculated in this way. Accurate measurements of the gas evolution could not be obtained for the experiments in very dilute solutions.

The above experimental method of determining dI_2/dt is subject to several possible inaccuracies; among the most obvious are loss of carbon tetrachloride by vaporization, irregularities in the transfer of iodine from the aqueous to the carbon tetrachloride layers, excessive heat losses due to the vaporization of carbon tetrachloride and of water, inaccuracies incident to the extremely rapid use of pipets, losses of iodine during washings, and iodate contamination in the iodine titrations. The loss of carbon tetrachloride by vaporization was shown to be negligible at 50°, small at 60° and so large at 70° that the temperature of a reaction mixture containing carbon tetrachloride and immersed in a thermostat at 70° could not be maintained above 68°. Accurate experiments at 70° were therefore impossible. Irregularities, for which no better reason could be given than that they were due to corresponding irregularities in the transfer of iodine from the aqueous to the carbon tetrachloride layer, sometimes appeared in the values of dI_2/dt obtained in the course of a run; the value of the over-all average dI_2/dt for such a run was almost always satisfactory, so that these fluctuations could be neglected. Pipet inaccuracies cancel out almost entirely if several samples are taken in the course of an experiment. Iodine losses by contact with aqueous layers, bath during reaction and in the subsequent washing, were approximately compensated by an addition of 3% to the volume of thiosulfate solution used. Iodate contaminations

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[3] In experiments requiring a sample to be taken every minute, this interval was shortened to five seconds.

[4] Liebhafsky, THIS JOURNAL, 53, 165 (1931).

were practically eliminated by three careful washings. No correction was made for concentration variations occurring during a run. The induction period[6] was never included in the time interval over which the over-all rate for an experiment was calculated.

The detailed data for a regular experiment (No. **023)** and for an irregular experiment (No. 09) are given in Table I.

TABLE I

THE CALCULATION OF RATE CONSTANTS FROM EXPERIMENTAL OBSERVATIONS

Experiment 023 Table III. Concentrations: $(H^+) = 0.0357$; $(IO_3^-) = 0.1001$; $(H_2O_2) = 0.0228$

Time, min.	0.1 *N* $Na_2S_2O_3$, *cc.*	*Cc.* of 0.1 *N* $Na_2S_2O_3$/min
1	0.0123	0.0154
2.5	.0045	.0017
6	.0067	.0020
10	.0080	.0020
28	.0416	.0028
61	.0626	.0020

Over-all average: $$\frac{0.0067 + 0.0080 + 0.0416 + 0.0626 + \frac{0.0626 - 0.0045}{4}}{58.5}$$

$= 0.1334/58.5 = 0.00228$ cc. of 0.1 N $Na_2S_2O_3$/min.

$dI_2/dt = 5(10^{-5}) \times 2.28(10^{-3}) = 1.14(10^{-7})$ moles of I_2/min.

Experiment 09, Table IV. Concentrations: $(H^+) = 0.1438$; $(IO_3^-) = 0.1001$; $(H_2O_2) = 0.746$

Time, min.	0.1 *N* $Na_2S_2O_3$, *cc.*	*Cc.* of 0.1 N $Na_2S_2O_3$/min.
0–0.75	0.15	0.27
0.75–4	.36	.13
4–7	.58	.21
7–10	.84	.30
10–14	.98	.26

Over-all average: $2.97/13.25 = 0.224$ cc. of 0 1 *N* $Na_2S_2O_3$/min.

$dI_2/dt = 11.2(10^{-6})$ moles I_2/min.

In this table and throughout this paper all concentrations will be given in moles/liter at room temperature, and will be indicated by ( ). All rates will be given in moles/min. for a 150-cc. reaction mixture. The temperature of all experiments was 50°, unless otherwise noted. The calculations of the rates for the first two intervals in Experiment 023 were made in the following manner

$$0\text{–}1 \text{ min. } \frac{0.0123 + \frac{0.0123}{4}}{1} = 0.0154; \quad \frac{0.0045 + \frac{0.0045 - 0.0123}{4}}{1.5} = 0.0017$$

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[6] The initial deficiency of iodine during the induction period will be discussed later. In several experiments at very low (H_2O_2), such as Experiment 023, Table I, formation of a relatively large amount of iodine was observed shortly after mixing the reagents; since this abnormality was variable and unreproducible, it was also disregarded in computing the over-all average.

The factor $\frac{1}{4}$ which appears in the numerator is necessary because 5 cc. of carbon tetrachloride always remained in the reaction vessel when 20 cc. was withdrawn for analysis of the iodine content.

Calculation of the Rate Constants. —Experiments, of the kind just outlined, were carried out to determine the order of the reaction with respect to (H^+), (IO_3^-) and (H_2O_2). Since two of these three concentrations were kept constant in each of the three series, it is possible to obtain three average values of the specific reaction rate by plotting the experiments of each of the three series. The constant concentrations used were (with a few exceptions): $(H^+) = 0.0357$, $(IO_3^-) = 0.1001$, $(H_2O_2) = 0.514$. The data are summarized in Tables II, III and IV; the concentrations and the corresponding values of dI_2/dt are given in the first portions of the tables. The other data will be discussed later.

TABLE II (SEE FIGURE 1)

VARIATION OF RATE WITH CHANGE IN (IO_3^-)

$(H_2O_2) = 0.514$; $(H^+) = 0.0357$; $T = 50°$

Expt.	(IO_3^-)	dI_2/dt (10^6)	"Defect" moles I_2 (10^6)	dO_2/dt (10^5)	Ratio $\frac{dO_2}{dt} / \frac{dI_2}{dt}$
027	0.00192	0.045	0.16	..	..
026	.0100	.270	1.6	0.90	33
012	.1001	2.73	10.8	2.01	7.4
025	.2301	6.29	33.5	4.61	7.0

TABLE III (SEE FIGURE 1)

VARIATION OF RATE WITH CHANGE IN (H_2O_2)

(R') $= 0.0357$; $(IO_3^-) = 0.1001$; T = 50°

Expt.	(H_2O_2)	dI_2/dt (10^6)	"Defect" moles I_2 (10^6)	dO_2/dt (10^5)	Ratio $\frac{dO_2}{dt} / \frac{dI_2}{dt}$
038	0.00217	0.011	..	..	..
024	.00874	.0473		..	..
023	.0228	.114		0.21	18.0
019	.0459	.243	..	.25	9.6
018	.250	1.40	2.7	.98	7.0
012	.514	2.73	10.8	2.01	7.4
061	.746	4.39	38.8	..	..
017	1.246	7.18	10.8	4.96	6.9
060	1.760	10.2	101.0	..	..
021	2.498	15.6	32.4	13.7	8.8

In Fig. 1, dI_2/dt of Tables II and III is plotted logarithmically against (IO_3^-), and against (H_2O_2): the logarithmic plot is used in order that the entire concentration range may be included in a plot of convenient size, and in order that the fundamental nature of relative, rather than absolute, changes in the concentrations of reacting substances may be emphasized. The radius of the circles used is equivalent to a 5% change in log dI_2/dt, the approximate magnitude of the average experimental error. The upper limit of the IO_3^- concentration range is fixed by the solubility limit of potassium iodate. The two straight lines show that the reduction of iodate ion is accurately first order with respect to (IO_3^-) over a 120-fold concentration range, and with respect to (H_2O_2) over a 1200-fold concentration range. In a plot of this kind, a set of experimental results must meet two requirements in order that the reaction involved may be first order with respect to the reactant considered: (1) the points must lie on a straight line; (2) the line must have a slope of 45°.[6] The lines in Fig. 1 meet both requirements.

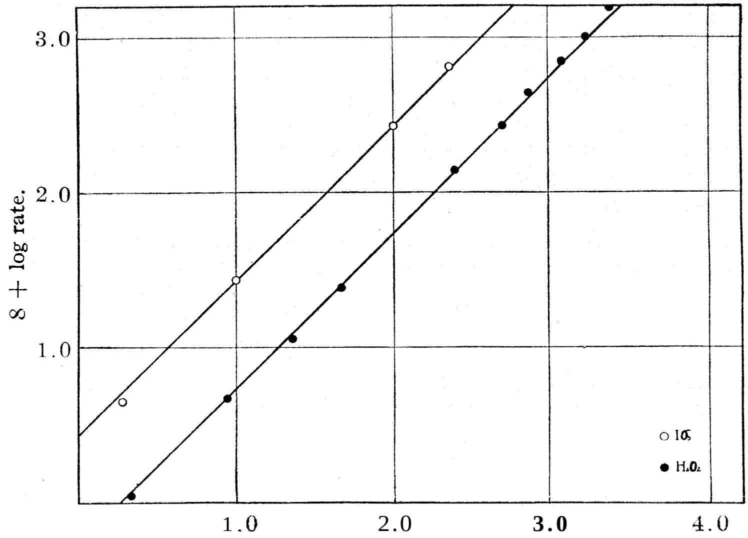

Fig. 1.—Variations of log dI_2/dt with log (IO_3^-) and with log (H_2O_2) (see Tables II and III).

In Fig. 2, dI_2/dt from Table IV for the various temperatures employed is plotted directly against (H^+). The radius of the circles now corresponds to a 5% error, only at (H^+) = 0.05 for the 50° experiments. Given the results from Fig. 1, it is evident that at the constant values of (H_2O_2) and (IO_3^-) employed, dI_2/dt obeys the following rate law at all hydrogen-ion concentrations below 0.14 N

$$dI_2/dt = k_1\,(H_2O_2)\,(IO_3^-) + k_2\,(H^+)\,(H_2O_2)\,(IO_3^-) \qquad (3)$$

The value of k_1 is obtained by dividing the intercept by $(H_2O_2)(IO_3^-) = 0.0514$; the result at 50° is $k_1 = 1.00(10^{-6})/0.0514 = 19.4(10^{-6})$. Simi-

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[6] The logarithmic method employed in this paper is useful in determining the order of a reaction with respect to any reactant so long as the concentrations of all other substances are (sensibly) constant; the slope of the line in such a plot is numerically equal to the quantity sought.

TABLE IV (SEE FIGURE 2)

VARIATION OF RATE WITH CHANGES IN (H^+) AT DIFFERENT TEMPERATURES

(a) At 50°

Expt.	(H^+)	(IO_3^-)	(H_2O_2)	$\frac{dI_2}{dt}$ (10^6) Meas.	calcd.	"Defect" moles I_2 (10^6)	$\frac{dO_2}{dt}$ (10^5)	Ratio $\frac{dO_2}{dt} / \frac{dI_2}{dt}$	% Yield of I^-
053	Initially neutral	0.1001	0.514	1.18		..	..	..	22
05	0.00716	.1001	.514	1.33		6.5	1.25	9.4	
011	.0214	.1001	.514	2.02		7.0	1.39	6.9	
012	.0357	.1001	.514	2.73		10.8	2.01	7.4	
013	.0439	.1001	.514	3.03		11.9	2.05	6.7	
014	.0572	.1001	.514	3.42		12.4	2.48	7.3	
04	.0715	.1001	.514	4.43		10.8	3.14	7.1	
016	.0929	.1001	.514	4.88		15.1	3.81	7.8	
08	.1072	.1001	.514	6.74		..	4.20	6.2	
015	.1438	.1001	.514	5.52	8.14	..	10.5	19	
06	.7144	.1001	.514	.465	36.4	..	41.4	890	
09[a]	.1438	.1001	.746	11.2	11.8	..	46.9	39	
010	.3564	.1001	2.498	33.1	90.9	..	375	113	
028	.2134	.2406	.746	8.77	40.4	..	..	..	

[a] Since the rate is proportional to (H_2O_2), $dI_2/dt = 11.2\ (10^{-6})$ at $(H_2O_2) = 0.746$ corresponds to $dI_2/dt = 7.74\ (10^{-6})$ at $(H_2O_2) = 0.514$; this is the value plotted in Fig. 2.

(b) At 60°: $(IO_3^-) = 0.1001$; $(H_2O_2) = 0.514$

Expt.	(H^+)	$\frac{dI_2}{dt}$ (10^6)	% Yield of I^-
049	Initially neutral	4.22	38
051	0.0214	6.93	
052	.0357	9.47	
050	.0715	14.7	
	(c) At 40°: $(IO_3^-) = 0.1001$; $(H_2O_2) = 0.514$		
056	Initially neutral	0.298	8 8
055	0.0214	.613	
054	.0357	.793	
039	.0715	1.32	
	(d) At 30°: $(IO_3^-) = 0.1001$; $(H_2O_2) = 0.514$		
058	Initially neutral	0.064	8.5
041	0.0357	.200	
057	.0572	.264	

larly the value of k_2 is obtained by dividing the slope of the line by (H_2O_2) (IO_3^-); at 50°, $k_2 = 48.7(10^{-6})/0.0514 = 947(10^{-6})$.

Values of k_2 can be computed from Fig. 1 only if k_1 is known; the calculation for the series in which (H_2O_2) varies will be given. Equation 3 after transposing and after substituting the numerical values of $k_1(IO_3^-)$ and (H^+) becomes: $(dI_2/dt)/(H_2O_2) = [19.4(10^{-6}) + k_2(0.0357)1.1001.$ For any point on the lower line in Fig. 1, the difference between ordinate and abscissa is simply $(\log dI_2/dt) - \log (H_2O_2) = \log (dI_2/dt)/(H_2O_2)$;

its numerical value is 0.743–6. The antilogarithm of this number, 48.7-(10^{-6}), is the ratio $(dI_2/dt)/(H_2O_2)$. Solving the above equation for k_2, we obtain $k_2 = 1005(10^{-6})$.

From the (IO_3^-) plot $(dI_2/dt)/(IO_3^-) = 27.3(10^{-6})$, whence the value $k_2 = 934(10^{-6})$ is calculated.

Since the values of k_2 are in substantial agreement, $k_2 = 965(10^{-6})$ may be taken as a reliable mean, and the value $k_1 = 19.4(10^{-6})$ may be regarded as satisfactory; k_1, however, is less accurate than k_2.

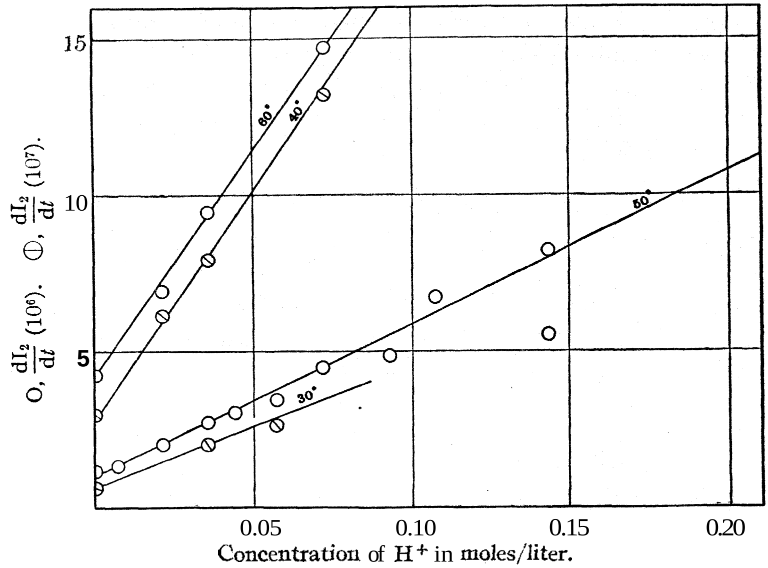

Fig. 2.—Variation of rate with (H^+) (see Table IV).

These constants must finally be multiplied by 2 to change from dI_2/dt to $-dIO_3^-/dt$, and by $6^2/_3$ to change from moles/min./150 cc. to moles/-min./liter. Equation 3 now becomes

$$-d(IO_3)^-/dt = 2.6\,(10^{-4})\,(H_2O_2)\,(IO_3^-) + 129\,(10^{-4})\,(H^+)\,(IO_3^-)\,(H_2O_2) \quad (4)$$

$-d(IO_3)^-/dt$ thus calculated is probably accurate to *5%.

Mechanism of the Reaction.—Equation 3 shows that the first step in the reduction of iodate may occur in the following ways

$$IO_3^- + H_2O_2 \longrightarrow IO_2^- + H_2O + O_2 \quad (5)$$

$$IO_3^- + H_2O_2 + H^+ \longrightarrow HIO_2 + H_2O + O_2 \quad (6)$$

The formation of IO_2^- and HIO_2 as intermediate products resulting from two simultaneous reactions appears to be the only simple explanation of the empirically determined rate law. This mechanism is not intended to exclude the possibility of the formation of intermediate complexes, such as $H_2O_2{\cdot}IO_3^-$ in Equation 5; there is thus no contradiction between this formulation and that of Bronsted for similar reactions.

The relatively rapid follow reactions cannot be postulated with certainty. As guides in selecting them we have the following. (1) Characteristic of iodine chemistry is the relatively rapid establishment of the equilibrium

$$I_2 4 H_2O \rightleftharpoons I^- + H^+ + HIO \qquad (7)$$

(2) Reactions involving the oxidation of hydrogen peroxide are generally first order with respect to that substance. **(3)** The oxidations of hydrogen peroxide by the hypo-halites and their acids are known to be rapid reaction~. (4)~The end-product of the reduction of iodate ion is iodine in acid, iodine and iodide ion in neutral, and iodide alone in basic solution.[7] (5) The reduction of iodous acid by hydrogen peroxide, if it occurs at all, is not very rapid.[8] Reaction between HIO_2 and I^- is very probable.

The reactions in acid solution following those in Equations 5 and 6 may therefore be the following

Formation of HIO_2	$H^+ + IO_2^- = HIO_2$	(8)
Second step in the reduction	$HIO_2 + H^+ + I^- = 2HI0$	(9)
Third step in the reduction	$HI0 + H_2O_2 = I- + H^+ + H_2O + O_2$	(10)
Formation of iodine	$HIO + I- + H^+ = H_2O + I_2$	(11)

Equation 1 is the sum of 6 (or 5 and 8) counted twice, 9 counted twice, 10 counted three times and 11. If the iodine concentration is permitted to build up in the hydrolysis equilibrium, the concentration of intermediate products increases, and the catalytic decomposition of hydrogen peroxide, which depends on the intermediate products such as I–, also increases.

The relative rates of the above reactions as individuals cannot be established. **A** comparison of their velocity as a group with the velocity of the first step is possible if the combined concentration of all iodine compounds intermediate between iodate and iodine is known; for, in a series of consecutive reactions which has reached a steady state, the concentration of an intermediate product is inversely proportional to the specific rate constant for the step in which this intermediate product is consumed.

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[7] The percentages of iodine obtained as I^- in the various experiments in neutral solution are given in Table IV. **An** experiment in which the initial (H^+) was **3** (10^{-12}) yielded only I–; quantitative work here was futile because of the large loss of hydrogen peroxide due to catalysis decomposition. Since, however, the reaction mixtures initially neutral were distinctly basic at the end of the run, their agreement with the rate law may be taken as an indication that this rate law is valid in moderately basic solution.

While the percentages of I^- at the different temperatures cannot be correlated because (H^+), (I_2) and (HIO) were not always the same, it may be pointed out that larger percentages of I^- at the higher temperatures are to be expected if the hydrolysis equilibrium, Equation **7,** is realized, from the sign of A H for this reaction.

[8] The reduction of iodous acid by hydrogen peroxide and by I^- has been discussed in Part I; it was there concluded that in moderately acid solution the former must be negligible. While this is probably true also for solutions of low acid concentration, there is always the possibility that hydrogen peroxide may begin to reduce either HIO_2 or IO_2^- as the acid concentration is further decreased.

The Induction Period.—At the beginning of every experiment there exists a time interval during which the rate of formation of iodine differs from that given by Equation 3; this time interval is presumably necessary to establish the concentrations of intermediate products required for the reduction of iodate ion. The length of this induction period in acid solution[9] is roughly independent of the concentrations of hydrogen and iodate ions, and inversely proportional to the concentration of hydrogen peroxide; in many experiments it approximates seven minutes. Ordinarily dI_2/dt begins with a small initial value and gradually increases until the expected rate is reached.

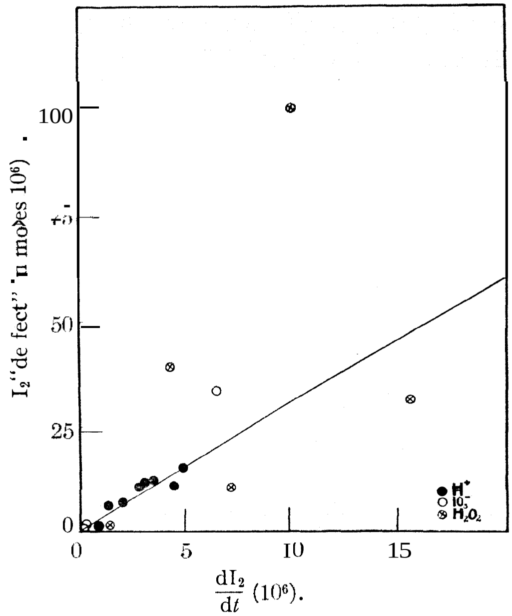

Fig. 3.—Variation of intermediate products with rate.

This induction period furnishes a means for calculating the maximum amount of iodine stored up as intermediate products in the course of any experiment. If the mechanism of the first step in the reduction of iodate is the simple one advanced above, then the rate of this first step is presumably always that calculated from Equation 3; the reduction of iodate ion according to this equation begins as soon as peroxide and iodate are mixed. If this simple picture is correct, the amount of intermediate products—the iodine "defect"—should be the difference between the average dI_2/dt for the experiment, multiplied by the time in minutes of the entire experiment, and the total amount of iodine actually obtained. The "defect" thus calculated is given in Tables II, III and IV, and is plotted against the rate in Fig. 3. Since the values of these "defects" depend upon the determination of very small amounts of iodine, the accuracy obtained is not very great. The legend shows, for any experiment, that substance the variation of whose concentration was principally responsible for the change in rate.

The calculations show, first of all, that the approximate percentage of

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[9] In neutral solution the induction period lengthened with decreasing iodate The formation here of amounts of I^- very large as compared with the amounts formed in acid solution is the explanation.

iodate stored up as intermediate products is 0.1%; the great speed of the follow reactions as compared to that of the first step in the reduction is thus established. The graph shows further that at low rates, the "defect" is proportional to the rate when (H^+) and (IO_3^-) are varied; the relationship expressed by the straight line is "defect" = 3 × rate. For variations in (H_2O_2) no such definite statement can be made; it may be concluded, however, that the "defect" is not independent of (H_2O_2) variations. The proportional increase of the concentration of intermediate products with the rate is to be expected as the result of any concentration change which increases the rate of the first step in the reduction of iodate without directly affecting the rate of the following reactions. The necessary increase of the absolute rate of the latter must then be brought about by an increase in the concentration of those intermediate products concerned. That the same proportionality which exists for (H^+) and (IO_3^-) does not exist[10] for (H_2O_2) justifies the selection of a reaction between HIO_2 and I^- as the second step in the reduction (Equation 9). If each step in the reduction involved one molecule of hydrogen peroxide, the "defect" should be unaltered when (H_2O_2) is changed.

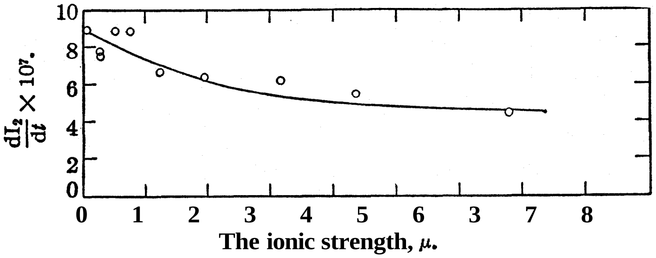

Fig. 4.—The salt effect.

The **Salt** Effect.—In Fig. 4 the result of a series of experiments on the salt effect at 60° is given. The experiments were carried out at (H^+) = (IO_3^-) = 0.038 M and (H_2O_2) = 0.115 M; changes in the ionic strength, μ, were produced by adding sodium nitrate.

We do not wish here to discuss the application of any "activity" theory of reaction rate. That there is a relatively small salt effect which disappears at higher μ is quite apparent; it is apparent further that no simple function of the activity coefficients involved is likely to yield a curve like that in Fig. 4. We must bear in mind, also, that this curve represents two salt effects, superimposed one upon the other, because the reaction has two rate-determining steps. One of these, the one involving only H_2O_2 and IO_3, should have a "linear' salt effect, but for the other the effect should be[11]

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[10] Experiment 012 serves as a point for all three cases.

[11] See Brönsted "The Velocity of Ionic Reactions," Contemporary Developments in Chemistry, Columbia University Press, 1927.

"exponential." The matter is complicated further by the change in solvent which occurs as the higher ionic strengths are reached, and by uncertainty of the value of activity coefficients under the experimental conditions. As evidence in dilute solution, where the activity rate applications have been most successful, the line in Fig. 1 representing (IO_3^-) variations might be used. There is a change in from **0.038** to **0.267** because of the change in (IO_3^-); but, as the graph shows, there is no salt effect greater than the experimental error.

Variation of Rate Constants with Temperature.—The effect on the rate constants of temperature variation in the interval from **30** to 60° is shown in Fig. **5**; the line of greater slope represents the value of k_1 as determined from the values of the intercepts in Fig. 2; the other line represents the values of k_2 as calculated from the slopes in that figure. From Fig. 5

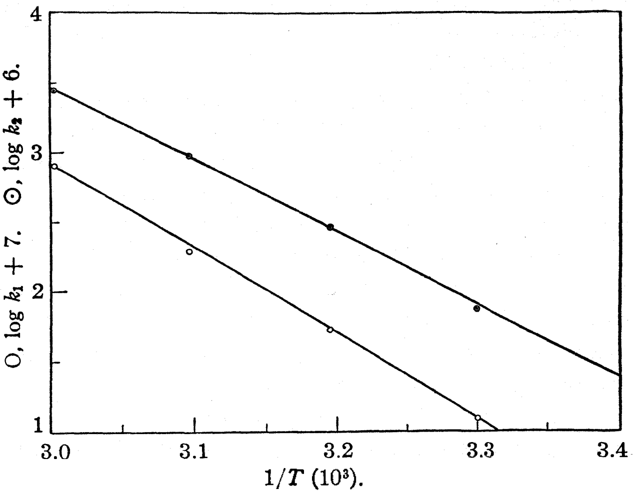

Fig. 5.—Variation of rate constants with temperature.

$$\frac{d \log k_1}{d\,(1/T)} = -6.07(10^3);\quad \frac{d \log k_2}{d\,(1/T)} = -5.20(10^3)$$

the corresponding values of the heats of activation are $Q_1 = 27{,}500 \pm 1500$ calories, and $Q_2 = 23{,}500 \pm 500$ calories. These values have been obtained by subtracting $RT/2$ calories (*ca.* 300 cal.) from the value calculated directly from the temperature coefficients, to correct for the variation of the root mean square velocity of the molecules with temperature. The estimated errors are the differences between the mean value of Q given above and the heats calculated from the lines of greatest and least slopes consonant with each set of experimental results in Fig. 5. **Using** the value of k_1 at 50° and the value of Q_1, the average of the diameters of H_2O_2 and IO_3^- may be calculated by the application of an **equation given** by Tolman;[12] for a heat of activation within the limits given above for Q, the value of the molecular diameter lies between $1(10^{-7})$ and $1(10^{-6})$ cm.

This average diameter is considerably larger than the values, 10^{-8} in order of magnitude, obtained from x-ray measurements; although a hydrated molecule in aqueous solution is probably larger than an ion in a crystal, the above result is larger than we should expect even for such a hydrated molecule. The simplified calculation we have made is, however, only very approximate. The number of moles colliding has been calculated for a gaseous system; if this number is greater for an equally concentrated aqueous solution of the reactants, then a smaller average diameter would be obtained. If, on the other hand, all collisions between molecules whose combined energies equal or exceed the minimum energy required for reaction are not effective, and an "orientation factor" must be introduced, the calculation would lead to an even larger molecular diameter. However, these difficulties will not vitiate the comparison to be made below, since the reactions to be compared are part of the same reaction system.

Using $5(10^{-7})$ as the average diameter, the rate may be calculated at which a bimolecular reaction involving IO_3^- and H_2O_2 with a heat of activation equal to Q_2 should proceed. **A** comparison of the rate thus calculated with that observed for Reaction 6 shows that the former rate is only about ten times the latter. This reaction, therefore, is too rapid to be the result of ordinary triple collisions;[13] it can be regarded simply as a bimolecular reaction in which the substance reacting with H_2O_2 is a complex, $H^+ \cdot IO_3^-$,[14] resulting from loose coupling, perhaps of an electrostatic nature, between the ions. Thus HIO_3, although completely dissociated in a thermodynamic sense, might act as a unit in chemical reactions involving both H^+ and IO_3^-.

The fact that the values of Q_1 and Q_2 are so nearly equal indicates that the activation processes in the two reactions are closely related. The dif-

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[12] Tolman, "Statistical Mechanics, Etc.," Chemical Catalog Co., 1927, p. 242, Equation 543; no. of mols. colliding/cc./sec. $= 10^{28.4427}\sigma^2 C_1 C_2 \sqrt{T\frac{M_1 + M_2}{M_1 M_2}}$; C_1 and C_2 are concentrations in moles/cc.; σ is the average diameter of the colliding molecules, T the absolute temperature and M_1 and M_2 are the ordinary molecular weights. This total number of moles colliding multiplied by the factor $e^{-Q/RT}$ which is the probability that any collision will have the minimum energy required for reaction, is equated to the experimentally measured rate; the equation is then solved for the value of σ.

[13] Since orientation is assumed to be of relatively greater importance in a triple collision, the introduction of orientation factors into the calculations would strengthen this conclusion.

[14] Another possibility would be complex formation of the type $H_2O_2 \cdot H^+$; this oxonium compound, however, can be present only at very low concentrations, since preliminary transference and freezing point experiments failed to show any evidence for its existence.

ference in the heats of activation, however, exceeds the estimated error. If we postulate the addition compounds, $H_2O_2{\cdot}IO_3^-$ and $H_2O_2{\cdot}HIO_3$, as intermediate steps in Reactions 5 and 6 it is evident that the presence of H^+ in the addition compound lowers the critical energy necessary for the reduction of iodate by 4000 calories. This is equal in order of magnitude to the heat of dissociation of a weak acid, such as HIO_2 by analogy appears to be. The products assumed in Reactions 5 and 6 are IO_2^- and HIO_2, respectively, and the difference in critical energies may thus be related to the energy of the H^+—IO_2^- bond. Whether this suggestion is of value can be determined by applying it, whenever accurate data for temperature coefficients are available, to other similar pairs of reactions, such-as those involved in the oxidation of iodide ion by H_2O_2 (cf. Part I, Equations 6a' and 6a).

Catalysis **and** the Rate Measurements.—Equation 1 suggests that the rate of the reduction involved might be followed by measuring either the rate of formation of iodine, or the rate of evolution of oxygen. In the ideal case

$$-\frac{dIO_3}{dt} = 2\frac{dI_2}{dt} = \frac{2}{5}\frac{dO_2}{dt} = -\frac{2}{5}\frac{dH_2O_2}{dt} \qquad (12)$$

If, however, hydrogen peroxide *oxidizes* any iodine compound present in the reaction system, Equation **3** will no longer be strictly valid; should such oxidation increase until one molecule of hydrogen peroxide reacted thus for every molecule reducing an iodine compound, the main reaction occurring in the system would be the sum of 1 and 2

$$10H_2O_2 = 10H_2O = 5O_2;\quad \Delta F^\circ = -250{,}900 \text{ cal., or}$$

$$H_2O_2 = H_2O + \frac{1}{2}O_2;\quad AF^\circ = -25{,}090 \text{ cal.} \qquad (13)$$

and a steady state analogous in principle to that in the simpler bromine–bromide catalysis[15] would then have been reached. In this event

$$-\frac{dIO_3^-}{dt} = 2\frac{dI_2}{dt} = 0 \text{ (very nearly)};\quad \frac{dO_2}{dt} = \frac{1}{2}\frac{dH_2O_2}{dt} \qquad (14)$$

The criterion for pure stoichiometric reduction of iodate is therefore $(dO_2/dt)/(dI_2/dt) = 5$, while for pure catalytic decomposition of hydrogen peroxide this ratio approaches an infinite value. Any system composed initially of iodate ion and hydrogen peroxide in acid solution must have for its rate-ratio a value included within the above limits. While the pure reduction of iodate has never been experimentally realized, pure catalysis will take place in every reaction system as soon as the steady state concentration of iodine has been built up by the reduction of iodate ion. Since, in moderately acid solution and at low (H_2O_2), this steady state iodine concentration is less than 10^{-6} *M*, it is experimentally impossible to study the reduction of iodate ion under such conditions.

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

As long as appreciable catalysis does occur, dO_2/dt can never accurately measure $-dIO_3/dt$, for a measurement of oxygen evolved must necessarily include oxygen produced by catalysis. That it is possible to have catalysis and still measure accurately $-dIO_3/dt$ by following dI_2/dt will now be shown. Experimental evidence proves that the reactions underlying Equation 1 must form a consecutive series which depends for its existence upon a series of intermediate iodine compounds; the slowest member of this series (*i. e.*, the one with the smallest specific rate) is the one directly involving iodate ion. If catalysis involving the oxidation of an intermediate compound back to iodate occurs, then some iodate will of necessity take part more than once in this slowest step. Under such conditions no measure of the absolute rate of reduction of iodate is possible, for there is no way of measuring how much of this substance, once reduced to a lower valence, is returned to its original state by the oxidizing action of hydrogen peroxide. Catalysis in which no iodate ion is re-formed, such as that resulting from the oxidation of I^- by H_2O_2, will not sensibly affect dI_2/dt, for it does not affect the *slowest reaction* taking place in the system.

A direct proof that no iodate is formed in the system is impossible. If, however, the amount of catalysis taking place as measured by the ratio $(dO_2/dt)/(dI_2/dt)$ changes from experiment to experiment, then the amount of oxidation involved in this catalysis must also change, as must the concentrations of all the intermediate products concerned. Thus, if the catalysis involves the re-formation of iodate ion, a change in the amount of catalysis will effect a change in the amount of iodate ion formed in the system, with the result that dI_2/dt (which must always measure the net amount of iodate reduced, since the concentration of intermediate products is small) will no longer follow a simple law.

A measure of the relative amount of catalysis in an experiment is the difference between the experimental value of $(dO_2/dt)/(dI_2/dt)$ and 5, its value for the pure reduction of iodate ion. In Tables II, III and IV these ratios are given wherever dO_2/dt was measured; with two exceptions, the values lie between 6.2 and 9.6 for all experiments with $(H^+) < 0.14$. (In the experiments on the salt effect three ratios between 5.9 and 6.6 were obtained.) In this region of acid concentrations, the amount of catalysis varies while dI_2/dt obeys the simple rate law in Equation 3; we conclude, therefore, that in this region the catalysis does not involve the re-formation of iodate ion.

In Table IV, the results of several experiments in more acid solutions are presented; the ratios for these experiments were always larger, 19 to 890, and calculations showed that the experimental values of dI_2/dt were always below those calculated from the simple rate law (see Columns 5 and 6, Table IV). The only simple explanation seems to be that catalysis at these higher acid concentrations involves some re-formation of iodate.

In Experiment 06 (Table IV), in which $(H^+) = 0.7144$, the value **890** for the ratio was obtained in the usual way with carbon tetrachloride; the value 160 was obtained by using mercury to extract the iodine. Since the extraction by means of mercury is more complete, the experiment definitely indicates that, other things being equal, the amount of catalysis depends on (I_2).

In the series of experiments at 50° plotted in Fig. 2, the low results can all be explained as due to catalysis involving IO_3^-. The most striking case is furnished by the two experiments at $(H^+) = 0.1438$ (Experiments **09** and 015, Table IV) which differ only in the magnitude of (H_2O_2). From unpublished work on the catalytic decomposition of hydrogen peroxide by iodic acid, it is known that the steady state (I_2) is proportional to (H_2O_2). That the experiment at the higher (H_2O_2) gives a value of dI_2/dt in agreement with the rate law is thus due to the effective elimination of IO_3^- formation made possible by the higher value of the steady state (I_2). Attempts further to extend the range of (H^+) for which Equation **3** is valid by increasing (H_2O_2) and (IO_3^-), failed.

The close relation of the reduction of iodate ion to the general problem of the catalytic decomposition of hydrogen peroxide by the iodine–iodate couple must now be apparent. A knowledge of the mechanism and the rate of this reduction will be of value first of all in interpreting the induction period for the catalysis, for the reduction of iodate was studied merely by prolonging this induction period indefinitely through the addition of carbon tetrachloride to remove the iodine formed.

In conclusion I desire to thank Professor William C. Bray for his assistance in this investigation.

Summary

1. The rate of reduction of iodate ion by hydrogen peroxide has been measured and found to be given by the expression $-d(IO_3)/dt = 2.6(10^{-4})(H_2O_2)(IO_3^-) + 129(10^{-4})(H^+)(IO_3^-)(H_2O_2)$ to within ±5%.
2. A plausible mechanism for the reaction has been suggested.
3. The induction period has been studied and discussed.
4. A relatively small salt effect has been found for the reaction.
5. The reaction has been studied from **30** to 60°, and the data thus obtained were used to calculate the average diameters of H_2O_2 and IO_3^-; the resulting value was of the correct order of magnitude.
6. The relation of this reaction to the catalytic decomposition of hydrogen peroxide by the iodine-iodate couple has been discussed.

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[CONTRIBUTION FROM THE BIOCHEMIC DIVISION, BUREAU OF ANIMAL INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

THE INFLUENCE OF P_H UPON THE FORMATION AND DECOMPOSITION OF THE CHLORO DERIVATIVES OF AMMONIA

BY ROBERT M. CHAPIN

RECEIVED DECEMBER 5, 1930 PUBLISHED MARCH 6, 1931

The Chloro-amines under Decreased P_H.—The writer[1] demonstrated that in aqueous solution maximum purity is reached by monochloro-amine (NH_2Cl) above P_H 8.5 and by dichloro-amine ($NHCl_2$) at P_H 4.5–5.0. In Fig. 1 are shown percentage recoveries of available chlorine from such solutions of the chloro-amines, containing an excess of ammonium ion, subjected to decreased P_H. Each atom of constituent chlorine in all three chloro derivatives (including nitrogen trichloride), as in hypochlorite, liberates two atoms of available chlorine under the methods of assay employed.[2] Evidently the P_H ranges of maximum stability coincide with the ranges of maximum purity. Under current hypotheses[3] the curves of Fig. 1 would be explained through the operation of pairs of competing reactions, e. g., $2NH_2Cl + HCl \longrightarrow NH_4Cl + NHCl_2$ and $3NH_2Cl \longrightarrow NH_4Cl + N_2 + 2HCl$, catalyzed by acid. But each of these reactions may be complex; the second, in particular, inasmuch as it is also catalyzed by alkali,[4] leaves the mechanism obscure.

The action of excess hypochlorite upon ammonium ion is known to progress to the formation of nitrogen trichloride. Stoppage of the chlorination at the stage of either chloro-amine demands, first, a limited proportion of the chlorinating agent, and, second, a sufficiently high P_H. Supplementing these established facts, the writer finds two fundamental general hypotheses adequate to account for the various products and decompositions which result from the chlorination of ammonium ion over a wide range of conditions: Hypothesis I. Under the influence of hydrogen ion, all three chloro derivatives of ammonia yield ammonium ion and hypochlorous acid. Hypothesis II. Under the influence of hydroxyl ion, all three chloro derivatives of ammonia yield chloride ion, the consequent oxidation of the residual atoms leading to a variety of associated products.

The first hypothesis was implied by Marckwald and Wille[4] in accounting for the production of nitrogen trichloride from acidified monochloro-amine, data regarding dichloro-amine not being in their possession. The

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[1] R. M. Chapin, THIS JOURNAL, 51, 2112 (1929).

[2] Preparative and analytical methods are described under the section on Experimental Technique.

[3] M. Bodenstein, *Z. physik. Chem* , Aht. A , 137, 131 (1928).

[4] W. Marckwald and M. Wille, *Ber.*, 56, 1319 (1023).

second is deduced from the apparently invariable presence of chloride ion among the decomposition products of all the chloro derivatives. The associated products include hypochlorite ion, nitrogen, nitrous oxide, nitrite and nitrate, which all have been identified by previous investigators.[5] Hitherto, however, practically nothing seems to have been available in the way of a quantitative study covering the alkaline decompositions of the chloro derivatives as a class.

Under Hypothesis I the formation of dichloro-amine through the acidification of monochloro-amine involves two steps. (A) $NH_2Cl + H^+ + H_2O \longrightarrow NH_4^+ + HClO$, and (B) $NH_2Cl + HClO \longrightarrow NHCl_2 + H_2O$.[6] The acidification of dichloro amine to below PH 4.4 similarly yields nitrogen trichloride. Inasmuch as no loss of available chlorine is indicated in these reactions, further discussion of Fig. 1 will follow a study of the influence of increased *PH* upon the individual chloro derivatives.

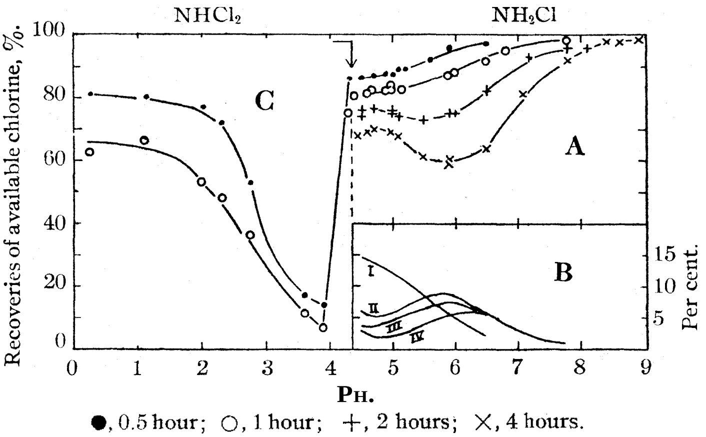

Fig 1. Recoveries of available chlorine at 25° from solutions of (A) NH_2Cl (0.01 N) and of (C) $NHCl_2$ (0.010 – 0.022 *N*) subjected to decreased PH. Fig 1-B.—Rate loss per 0.5 hour; from 1-A.

$NHCl_2$ and NCl_3 under Increased *PH*.—In Fig. 2-A are shown percentage recoveries of available chlorine from solutions of dichloro-amine, containing excess ammonium ion, subjected to increased *PH*. The residual substance above *PH* 9.0 was identified as monochloro-amine through its partition ratio, $C_{CHCl_3}/C_{Aq.}$[1] It was concluded that the principal reaction was (C) $2NHCl_2 + 4OH^- \longrightarrow 3Cl^- + ClO^- + 3H_2O + N_2$, under which 25% of the original available chlorine should be

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[5] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, 1928.

[6] Discussion of the electronic mechanism of chlorination being beyond the scope of this paper, the term hypochlorous acid (HClO) is here of comprehensive significance, without regard to possible ionization.

recoverable. But during one hour at *Ph* 9.6 oxy acids of nitrogen were developed equivalent to 3.0 p. p. m. of nitrogen, of which nitrite afforded 1.8 p. p. m. of nitrogen. These quantities are equivalent to 8.2% of the original available chlorine and therefore quantitatively account for the deficient recovery shown. Though the liberated ClO ion would rapidly react with excess ammonium ion present to produce monochloro-amine, there is experimental evidence for its evanescent existence. Thymol blue[7] is rather resistant toward both chloro-amines, but when *a* solution of dichloro-amine is treated with ammonia and thymol blue simultaneously, or in rapid succession, the color quickly fades after a transitory stage of abnormally bright blue.

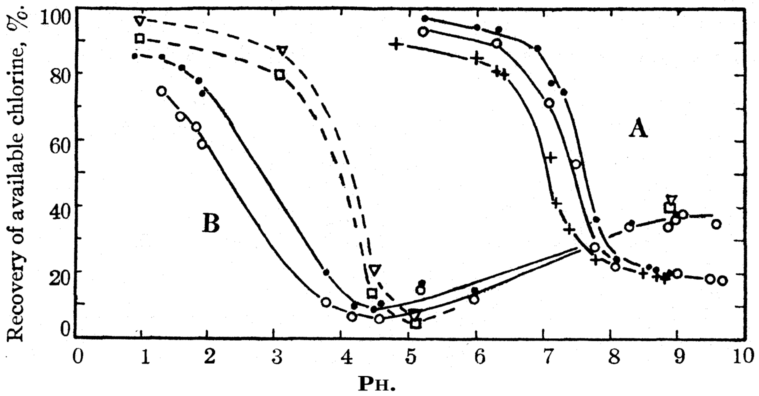

Fig. 2-B.—Nitrogen trichloride. Fig. 2-A.—Dichloro-amine.
At 25": ●, 0.5 hour; ○, 1 hour; +, 2 hours. At 7": V, 0.05 hour; ⊡, 1 hour.

Fig. 2.—Recoveries of available chlorine from solutions of $NHCl_2$ (0.01 *N*) and of NCl_3 (0.013 – 0.018 N) subjected to increased Ph.

Similar experiments on nitrogen trichloride subjected to increased Ph in the presence of ammonium ion are covered by Fig. 2-B, and monochloro-amine was similarly found to be residual at Ph 9.6, together with a small proportion of nitrite. It was concluded that the principal reaction at that Ph was (D) $2NCl_3 + 6OH^- \longrightarrow 3Cl^- + 3ClO^- + 3H_2O + N_2$, under which 50% of the original available chlorine should be recoverable. Failure to attain more than 40% recovery was attributed to rapid decomposition while the preparations were passing through the intermediate *Ph* range during the process of mixing the alkaline buffer with the original solution.

Comparison of Figs. 1 and *2* indicates that the effect of hydroxyl ion

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[7] Indigo carmine, employed by F. Raschig, *Chem.-Ztg.*, 31, 926 (1907). for the detection of hypochlorite in the presence of monochloro-amine is much less sensitive than either thymol blue or methyl orange,

is adequate to account for the curves shown in Fig. 1. When dichloro-amine is acidified (Fig. 1-C), the loss is not due to direct action of hydrogen ion upon that substance, but to the action of hydroxyl ion upon the resulting nitrogen trichloride. When monochloro-amine is acidified (Figs. 1-A and 1-B) the free liberation of hypochlorous acid under Equation A carries some molecules of chloro-amine through to nitrogen trichloride; consequently the curves represent combined decompositions of both nitrogen trichloride and dichloro-amine under the influence of hydroxyl ion.

In view of the work of Marckwald and Wille, decompositions of monochloro-amine were not studied.

Reason arose for doubting the apparently uncontradicted statement of Anderson[8] that the passage of chlorine into excess aqueous ammonia of varied concentration always affords a considerable proportion of oxygen at all stages. He reported 13.8% in the dried gas evolved from "strongest" ammonia water, but unfortunately gave neither his method of preparation of chlorine nor a test for its purity, nor assurance that the evolved gases were freed from ammonia. Here the chlorine was prepared from hydrochloric acid and specially made manganese dioxide, and showed only a trace insoluble in sodium hydroxide solution. About 75 cc. of the gases evolved from the chlorination of excess ammonia water, after standing for about one hour, was drawn into a gas buret. The confining liquid was normal sulfuric acid tinted with methyl orange. Thorough shaking in the buret left the pink unchanged, insuring absence of both ammonia and chloro derivatives from the gas measured. The absorbing agent for oxygen was alkaline pyrogallol, and the fitness of the absorption pipet was proved through a final assay of outdoor air. "Ammonium hydroxide, C. P., sp. gr. 0.90" was chlorinated at full, half, and quarter strengths, but in each case the gas lost less than 0.2% in the pyrogallol pipet, a proportion within the limits of error of the work. The residue from the evaporation of the ammoniacal liquid afforded a distinct diphenylamine test for nitrate in the run with quarter strength, but none in the run with full strength ammonia water.

Effects of Excess Chlorine.—In Fig. 3 are shown moles of available chlorine lost per mole of ammonium when similarly buffered solutions of known concentrations were mixed. At P_H 9 the mixtures evidently ran through rapid alternate formations of chloro derivatives and decompositions of the latter under the influence of hydroxyl ion, until either ammonium ion or hypochlorite was exhausted and only monochloro-amine and ammonium ion, or hypochlorite, remained, action being found already practically complete in one-quarter hour. Excess hypochlorite was detected after half an hour by the thymol blue test in the

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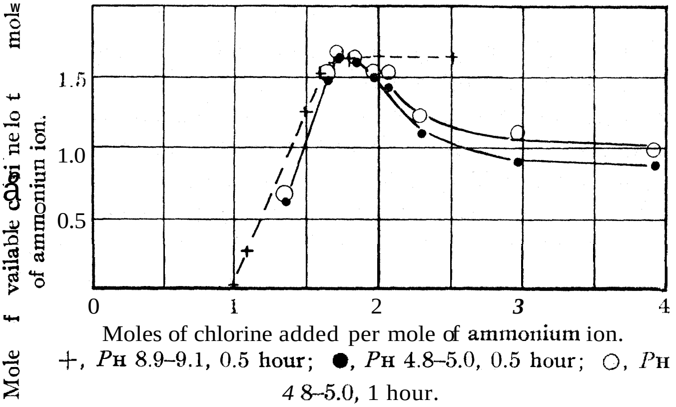
[8] Alfred Anderson, *Chem. News*, 5, 246 (1862).

mixture of mole ratio 1.7 but not in that of ratio 1.6. At PH 5 the mixtures ran through a similar series of decompositions up to a mole ratio of close to 1.7, but here excess of chlorine evidently inhibited the decomposition of nitrogen trichloride under the influence of hydroxyl ion. A mixture of mole ratio 3.45 lost only 57% of its potentially ammoniacal nitrogen in half an hour, as shown by concordant determinations after reduction with As_2O_3–HCl and with sulfurous acid.



+, PH 8.9–9.1, 0.5 hour; ●, PH 4.8–5.0, 0.5 hour; ○, PH 4.8–5.0, 1 hour.

Fig. 3.—Moles of available chlorine (Cl_2) lost per mole ammonium ion (0.005 *M*) after admixture at *PH* 9.0 and at *PH* 4.9, at 25°.

When, however, the reaction was effected in much higher concentration at PH 5 by letting a heavily buffered ammonium solution flow[9] into a gas buret charged at atmospheric pressure with pure dry chlorine, the mole ratio 1.5 was found to leave a trace of chlorine in excess. Accordingly, departure from the relation (E), $2NH_3 + 3Cl_2 \longrightarrow 6HCl + N_2$, appears to increase with dilution. In the dilute solutions at both PH 5 and PH 9, about 40% of the departure from the mole ratio 1.5 was accounted for by the formation of nitrate. Only questionable traces of chlorate or perchlorate were detected, so search was made for nitrous oxide.[10] Preparations of 500 cc., containing the equivalent of 0.005 M ammonium chloride, were made by letting solutions of sodium hypochlorite, acetic acid or boric acid, and buffered ammonium chloride, flow successively into a previously evacuated flask. After one hour the gases were pumped from the warmed flask into a mercury buret, washed successively with 1 to 2 cc. of strong sulfuric acid and potash over mercury in pipets, and measured over a little distilled water. Next they were run into an ordinary pipet filled with air-saturated distilled water, and the detached pipet was shaken for five minutes. After measurement, absorption was repeated with fresh

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[9] C. T. Dowell and W. C. Bray, THIS JOURNAL, 39, 896 (1917).

[10] Lord Rayleigh, *Proc. Roy. Soc.* (London), 64, 95 (1898).

water, which took out about one-tenth as much as the first treatment. A third treatment showed no significant change. At mole ratio 1.67, which by tests with methyl orange was sufficient to leave a trace of hypochlorite, two preparations at PH 5 afforded equivalents of 5.2 and 6.9 cc. of water-soluble dry gas at 0° and 760 mm., which quantities, reckoned as nitrous oxide, quantitatively account for the remainder of the available chlorine consumed. But at PH 9 no nitrous oxide was found at mole ratios 1.60 or 1.67, so that under conditions representing the storage of nitrogen trichloride at PH 9 there remains a quantitative deficit.

The formation of the oxy compounds of nitrogen noted above resembles the various decompositions[5] of hyponitrous acid, $H_2N_2O_2$. Accordingly, the following mechanism is suggested. First, the production of chlorohydroxylamines, NHClOH and NCl_2OH, by metathesis, as in Equation (F), $NCl_3 + OH^- \longrightarrow Cl^- + NCl_2OH$; second, the removal of chlorine and hydrogen chloride from these by further action of hydroxyl ion, leaving the nitroyl group, HNO, which finally affords the characteristic decomposition products. Kolotoff[11] found that sodium hypobromite oxidizes hydroxylamine to hyponitrite.

Equilibria of Nitrogen **Trichloride.**—In Fig. 4 are shown values for the partition ratio, $C_{CCl_4}/C_{Aq.}$, of the available chlorine in solutions of varying PH and containing excess ammonium ion, after being held for two hours at 25°. In the one series ammonium chloride was used and hydrochloric acid, with or without potassium chloride, was the acidifying agent below *P*H 1.8; in the other, ammonium sulfate, sulfuric acid and potassium sulfate were used instead. The $HI-Na_2S_2O_3$ method of assay was employed because of its superior delicacy. Evidently the points **A** and **A'** mark maximum purity of the resultant nitrogen trichloride. Incomplete reaction, or reversion to ammonium chloride, begins to appear in hydrochloric acid solutions a little stronger than normal and is nearly complete at 4 *N*, but none is indicated in sulfuric acid solutions up to 7 N, so that it cannot be due solely to low PH. The explanation of reversion given by Seliwanow[12] appears adequate. In aqueous solution nitrogen trichloride is in equilibrium with hypochlorous acid; (G), $NCl_3 + H^+ + 3H_2O \rightleftharpoons NH_4^+ + 3HClO$. In the presence of only sulfuric acid, even of high concentration, the small concentration of hypochlorous acid necessary to stabilize nitrogen trichloride is itself stable, so that reversion is scarcely perceptible; but in presence of sufficient hydrochloric acid the reaction (H), $HClO + Cl^- \rightleftharpoons OH^- + Cl_2$ may so reduce the actual concentration of hypochlorous acid that reaction (G) progresses toward the right to practical completion. It directly follows that chlorine itself is inert toward ammonium ion, chlorination occurring only when the concentration

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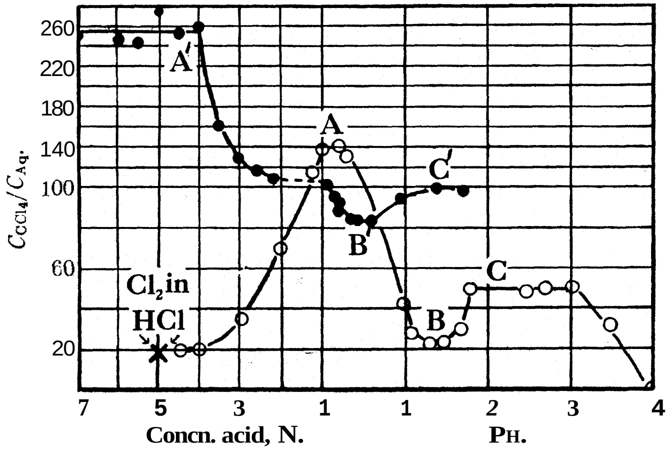
[11] S. S. Rolotoff, *J. Russ. Phys.-Chem. Soc.*, 23, 3 (1890), through Mellor, Ref. 5.

[12] T. Seliwanow, *Ber.*, 27, 1012 (1894).

of chloride ion is sufficiently low and the PH is sufficiently high to permit formation of the necessary concentration of hypochlorous acid.

In opposition to the foregoing, Noyes[13] suggests that the formation of all three chloro derivatives involves direct addition of either chlorine or hypochlorous acid, not to ammonium ion, but to ammonia, according to the scheme $NH_3 + Cl^+Cl^- \longrightarrow NH_3Cl^+Cl^- \longrightarrow NH_2Cl + H^+Cl^-$. Similarly, dichloro-amine would be derived from monochloro-amine, and finally nitrogen trichloride from dichloro-amine; but this scheme appears workable only in presence of free chlorine or hypochlorous acid. The writer does not see how the production of dichloro-amine and nitrogen trichloride from monochloro-amine through mere decrease of PH may be accounted for without violating Noyes' fundamental assumption that each chlorine atom retains its electronic configuration, its positive or negative character, unchanged throughout. Again, Noyes accounts for the effect of strong hydrochloric acid upon nitrogen trichloride by reversing the scheme of formation, thus, $NCl_3H^+Cl^- \longrightarrow NHCl_2 + Cl^+Cl^-$, until, after a similar passage through monochloro-amine, ammonium chloride is finally reached; but these chloro amines, and still more the corresponding chloro-ammonium chlorides, should be so comparatively little soluble in organic solvents that their presence in hydrochloric acid solutions somewhat stronger than *N* should be apparent from the partition data of Fig. 4. Lastly, the theory demands the existence of a significant concentration of ammonia in sulfuric acid solution as strong as 7 N. Altogether,



●, in sulfuric acid; ○, in hydrochloric acid.

Fig. 4.—Partition ratios, $C_{CCl_4}/C_{Aq.}$, of available chlorine in stored aqueous solutions of nitrogen trichloride. Initial chlorine, about 0.02 N.

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[13] W. A. Noyes, This Journal, 42, 2173 (1920).

the theory of Noyes appears to gain no support from the present experiments.

Returning to the discussion of Fig. 4, when the PH rises from the points A and A', the decreasing partition ratios indicate formation of another substance, but complete analyses of chloroform extracts from several preparations over the range A to C showed only nitrogen trichloride. The substance in question rather persistently resisted repeated extraction by carbon tetrachloride and traces of it powerfully bleached methyl orange. It was assumed to be simply hypochlorous acid, for Hypotheses I and II applied to Figs. 1 and 2 indicate a considerable range below *P*H 4.4 over which both the action of hydrogen ion upon dichloro-amine and the action of hydroxyl ion upon nitrogen trichloride should cooperate to maintain a relatively high concentration of hypochlorous acid.

The distinct dips in the curves at the points B and B' may perhaps be due to the presence of Cl_2O derived from the equilibrium (I) $2HClO \rightleftarrows H_2O + Cl_2O$, recently studied by Roth.[14] He found for Cl_2O the partition ratio $C_{CCl_4}/C_{H_2O} = 2.22$.

Experimental Technique

The buffers were various mixtures of phosphates (acid, middle and alkaline ranges), acetates and borates. The *PH* indicators were those recommended by Clark,[15] except that methyl orange replaced brom phenol blue, while cresol red (acid range)[16] was employed below the acid range of thymol blue. Nitrogen trichloride, when present, was extracted by carbon tetrachloride before the determination of *PH*, and, when necessary. residual bleaching powder was removed by adding to the test in the tube, before the indicator, one drop of potassium iodide solution, followed by 0.1 N sodium thiosulfate to decolorization. All *PH* results reported are those determined at the end of the various processes, and were, in most cases, slightly below the calculated initial PH.

The three chloro derivatives were prepared by rapid admixture of solutions of chlorine or hypochlorite and of ammonium ion, both buffered alike, the former, where practicable, being poured into the latter. Typical formulas were as follows: for monochloro-amine, (a) 15 cc. of 5% ammonium chloride solution, 50 cc. of 0.1 M sodium tetraborate, diluted to 100 cc., and (b) sodium tetraborate the same, 40 cc. of strong chlorine-water, diluted to 100 cc.; for dichloro-amine, (a) 20 cc. of 5% ammonium chloride solution, 32 cc. of 0.5 M sodium acetate, 8 cc. of 0.5 M acetic acid, diluted to 100 cc., and (b) sodium acetate and acetic acid the same, 60 cc. of chlorine-water; for nitrogen trichloride, (a) 20 cc. of 5% ammonium chloride solution, 5 cc. of 0.5 M hydrochloric acid, and (b) 25 cc. of chlorine-water, 20 cc. 0.5 M hydrochloric acid, diluted to 100 cc. The minimum periods of storage before use and the final *PH* were as follows: monochloro-amine, one hour, *PH* 9.0; dichloro-amine, two hours, *PH* 4.6–5.0; nitrogen trichloride, half an hour, *PH* 0.9.

For making changes of *P*H, sufficient solution of the chloro derivative was placed in a glass-stoppered, graduated cylinder in a water-bath, a sample for assay was pipetted out, then the remainder was immediately treated with the necessary acid or alkaline solution.

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[14] W. A. Roth, *Z. Physik. Chem.*, *145*, 289 (1929).

[15] W. Mansfield Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 2d ed., 1922.

[16] F. R. McCrumb and W. R. Kenny, THIS JOURNAL, 51, 1458 (1929).

Available chlorine in the two chloro-amines is determinable by the acid–iodide–thiosulfate method,' but in the presence of nitrite only sufficient acetic acid should be used to reach about PH 4. Dowell and Bray[8] reported neither iodide nor arsenious oxide as satisfactory for use in assaying nitrogen trichloride. Here it was found that about 80% of the total available chlorine of nitrogen trichloride was recoverable through a moderately acid solution of potassium iodide–hydrochloric acid from both aqueous and carbon tetrachloride solutions, and the method was employed in the presence of nitrogen trichloride in the single case of the work covered by Fig. 4. But arsenious oxide was found entirely reliable for all three chloro derivatives provided sufficient hydrochloric acid was present to effect reversion to ammonium chloride and chlorine before direct action upon arsenic trioxide occurred. A final concentration of not less than 20 volumes of the concentrated reagent per 100 of the final mixture appeared sufficient. Excess arsenic trioxide was titrated either by the bromate or the iodate method, depending upon whether the sample was in aqueous or organic solution. Solutions of pure nitrogen trichloride in chloroform afforded results closely in accord with determinations of ammonium and chloride ions made after reduction with aqueous sulfur dioxide.

The total nitrogen converted to oxy acids was determined by Nesslerization after reduction with aluminum.[17] Both sample and blank were first freed from active chlorine by the same proportions of identical solutions of potassium iodide and sodium thiosulfate, then to the blank was added acid or alkaline buffer corresponding to that already added to the sample. Just before the distillation of ammonia, each was treated with an alkaline lead solution to retain hydrogen sulfide arising from the reduction of thio acids. Nitrite nitrogen was determined colorimetrically by the A. P. H. A. method. Active chlorine was first removed by an aqueous solution of arsenic trioxide, after which the blank received the acid or alkaline buffer necessary to bring it into correspondence with the sample. The determinations noted under Fig. 3 were conducted similarly, the solution of ammonium ion there taking the place of the "buffer" referred to above.

Summary

Quantitative experiments lead to the following conclusions:

1. Elementary chlorine is inert toward ammonium ion, requiring conversion to hypochlorous acid before attack occurs.
2. Hydrogen ion induces formation of ammonium ion from each chloro-amine, particularly below a characteristic PH, the resulting hypochlorous acid then reacting to produce a more highly chlorinated derivative.
3. Hydroxyl ion induces formation of chloride ion from nitrogen trichloride or dichloro-amine, particularly above a characteristic PH, with gaseous nitrogen and hypochlorite ion as the principal associated products. With increasing dilution nitrous oxide, nitrite and nitrate also appear. To account for these oxy derivatives it is suggested that hydroxyl ion may first react by metathesis to produce chloro-hydroxyl-amines, which then decompose to afford the nitroyl group, characteristic of hyponitrous acid.
4. The statement that some gaseous oxygen is formed by passage of gaseous chlorine into ammonia water is apparently erroneous.

WASHINGTON, D. C.

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[17] "A. P. H. A. Standard Methods of Water Analysis," 3d ed., 1917.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 8]

THE SELENIOUS ACID METHOD FOR THE DETERMINATION OF ZIRCONIUM

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RECEIVED DECEMBER 18, 1930 PUBLISHED MARCH 6, 1931

The accurate determination of zirconium has always been a matter of considerable difficulty, especially in materials containing a variety of other metals. Many of the methods of analysis which have been proposed give good results when applied to simple zirconium compounds, but fail when certain other elements are present. The two most common methods have been the phosphate method and the cupferron method, both of which have been carefully studied by Lundell and Knowles,[1] who, in their proposed procedures, have made provision for the elimination of all interfering elements. The removal of such interfering elements in samples of moderate complexity, however, involves a very long series of manipulations.

Smith and James[2] have recently shown that the precipitation of zirconium by selenious acid can be applied to the quantitative determination of zirconium. They studied the effect of the presence of only a few interfering elements, however, and as J. W. Marden[3] has pointed out, however promising the method may seem, the effect of such metals as are ordinarily encountered in zirconium ores and alloys must be understood before the method can be generally used.

It was the purpose of this investigation, therefore, (a) to determine the most favorable conditions for the quantitative precipitation of zirconium selenite; (b) to determine what elements other than zirconium are precipitated by selenious acid under the conditions for the most favorable precipitation of zirconium; (c) to determine what elements are adsorbed or otherwise brought down by zirconium selenite in sufficient amounts to interfere with the accuracy of the estimation of zirconium; (d) to devise a reasonably rapid and direct method for eliminating the interfering elements and quantitatively precipitating the zirconium selenite in pure form; (e) to apply the method to mixtures and natural products containing zirconium in conjunction with a wide variety of other metals, especially those which have been found to cause interference.

Previous Work.—The formula of the flocculent precipitate obtained by the addition of selenious acid to solutions of zirconium salts is, according to Nilson,[4] $4ZrO_2{\cdot}3SeO_2{\cdot}18H_2O$. On heating the solution containing the

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[1] G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.*, 12, 562 (1920); THIS JOURNAL, 41, 1801 (1919); 42, 1429 (1920).

[2] M. M. Smith and C. James, *ibid.*, 42, 1764 (1920).

[3] J. W. Marden, *Bulletin* 212, Bur. of Mines, p. 310.

[4] A. Nilson, "Researches on Salts of Selenious Acid," University of Upsala, 1875.

suspended precipitate with excess selenious acid, the precipitate is slowly converted to the crystalline normal selenite, $Zr(SeO_3)_2$. Smith and James showed that the precipitation is quantitative and recommended that it be made from 500 cc. of solution containing 5% hydrochloric acid. Ignition of the precipitate gives zirconium dioxide and with equal amounts of original zirconium salt the weights of the dioxide are essentially the same as those obtained by the ignition of the corresponding cupferron and ammonia precipitates. Smith and James likewise found that aluminum and the rare earths do not interfere except that cerium must be in the cerous form, and also that the presence of amounts of iron usually present in zirconium ores does not affect the results. Titanium interferes but can be completely held in solution by hydrogen peroxide. Thorium also interferes but the writers state that this element is rarely a constituent of zirconium ores.

Experimental Work

Solutions Used.—A solution of C. P. selenious acid containing 100 g. per liter was prepared for use as a precipitant and several liters of zirconyl chloride solution were prepared of an approximate concentration of 12 g. of $ZrOCl_2 \cdot 8H_2O$ per liter. The zirconium from 25-cc. portions of the latter solution was precipitated (a) by cupferron from 10% sulfuric acid solution, and (b) by 20 cc. of selenious acid from 400 cc. of neutral solution.[5] The ignited precipitates gave the following values.

	Precipitation by cupferron, g. ZrO_2	Precipitation by selenious acid, g. ZrO_2
	0.1200	0.1200
	.1197	.1206
	.1199	.1194
		.1198
		.1200
		.1200
		.1201
Average	0.1199	0.1200

This zirconyl chloride solution was used throughout the entire investigation and its concentration was checked frequently.

Effect of Acid on the Precipitation of Zirconium Selenite.—Since in an ordinary analysis of zirconium it might be desirable to precipitate zirconium selenite from nitric acid or sulfuric acid solution, as well as from hydrochloric acid solution, and since considerable alkali salts might very likely be present from previous neutralizations, the effect of the presence and concentrations of these substances on the quantitative precipitation of

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[5] One-half milligram of zirconium in 500 cc. of solution acidified with hydrochloric acid gives a visible precipitate with selenious acid. This corresponds to 0.05% Zr in a one-gram sample of ore.

zirconium by selenious acid was next studied. The results are listed in Table I. In all the determinations a total volume of 400 cc. was used, *25* cc. of standard zirconyl chloride solution was present (equivalent to 0.1200 g. of ZrO_2), and the zirconium was precipitated from boiling solution with 20 cc. of 10% selenious acid solution. The precipitate was allowed to stand and was then filtered and ignited.

In these precipitations the use of hydrochloric acid or nitric acid gave immediate flocculent precipitates, which, on long standing (*e.* g., overnight) on the hot-plate, became more crystalline. The precipitates in the presence of sulfuric acid did not appear at once and in some cases did not begin to form before an hour or more. When they did appear, they were entirely crystalline in character and had a great tendency to adhere to the scratches on the beaker, from which they were removed only with difficulty, Furthermore, the two forms of precipitates differed markedly in their lease of solubility in acids. The amorphous form (basic selenite) was readily soluble in 6 *N* mineral acids, while the crystalline form (normal selenite) was difficultly soluble.

TABLE I

ZrO_2 present, 0.1200 g.

Acid	6 *N* acid present, cc.	Acid normality of solution	ZrO_2 found, g.	
HCl	40	0.60	0.1202	0.1199
			.1203	
			.1196	
			.1199	
			.1200	
			.1198	
			.1196	
	50	0 75	.1178	
	60	0 90	.1097	
	80	1.20	.0930	
HNO_3	10	0 15	0.1201	
	25	.38	.1201	
	35	.53	.1187	
	40	.60	.1151	
	50	.75	.1040	
H_2SO_4	40	.60	0.1206	0.1202
			.1198	
			.1200	
			.1200	
			.1205	
	60	0.90	.0142	
	80	1.20	.0080	

It is seen from Table I that greater acidity in hydrochloric acid can be used than in nitric acid if complete precipitation is to be expected, and that with hydrochloric acid the total acidity should not much exceed 0.6 *N*

(40 cc. of 6 N HCl in 400 cc. of solution). Sulfuric acid is the least desirable acid medium of the three, not only because of the slowness of precipitation and greater difficulty of removing the precipitate from the beaker, but also because a slight increase in acidity over 0.6 N causes a very sharp decrease in the amount of zirconium precipitated.

Incidentally, the statement made by Smith and James[6] that precipitated zirconium selenite cannot be easily redissolved for reprecipitation was found to apply only to the crystalline form. The freshly precipitated flocculent form dissolves in hot 6 N hydrochloric acid without much difficulty.

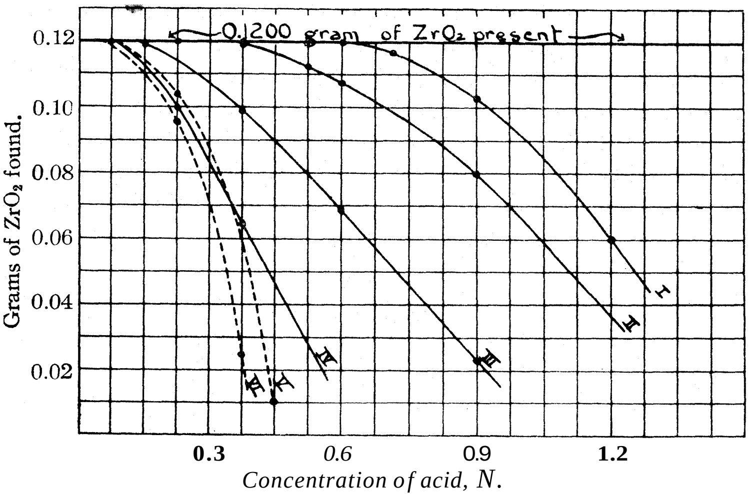

Fig. 1.—I, HCl + 0.5 *g. of* Na_2SO_4; II, *HCl* + **2** *g. of* Na_2SO_4; III, HCl + *5 g.* of Na_2SO_4; *IV,* HCl + *10* **g.** *of* Na_2SO_4; *V,* H_2SO_4 + *0.5* **g.** *of* Na_2SO_4; *VI,* H_2SO_4 + *2 g. of* Na_2SO_4.

Effect of Alkali Salts on the Precipitation of Zirconium Selenite.—Determinations of zirconium with selenious acid in the presence of alkali salts were next made In these experiments, 400 cc. of solution were used, 25 cc. of standard zirconyl chloride (equivalent to 0.1200 g. of ZrO_2) was present and the zirconium was precipitated from boiling solution with 20 cc. of 10% selenious acid. Varying concentrations of hydrochloric acid and of sulfuric acid were used and also varying. amounts of alkali salts. Several determinations using 40 cc. of 6 *N* hydrochloric acid and amounts of sodium chloride, sodium nitrate, ammonium chloride and ammonium nitrate up to 10 g. gave precipitates of zirconium selenite producing on ignition 0.1200 ± 0.0004 g. of ZrO_2. Similarly, the presence of alkali chloride showed no appreciable effect upon the precipitation from sulfuric acid solution. The presence of alkali *sulfate,* however, had a marked effect on the precipitation from hydrochloric acid solution, and an even

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[6] *Smith and James,* Ref. *2,* **p. 1768.**

greater effect from sulfuric acid solution. These effects are shown in Fig. 1, in which grams of ZrO_2 obtained are plotted against the volume of acid in 400 cc. of solution. From this graph it is seen that *increasing amounts of sulfate require a corresponding decrease in acidity for complete precipitation of zirconium.* Conversely, with *a* solution of desirable acidity in hydrochloric acid *(e. g., 0.6 N) only a small amount of sulfate can be present if complete precipitation is desired.*

In all cases, increasing amounts of alkali sulfate caused a decrease in the rate of precipitation and gave more crystalline precipitates.

Explanation of the Effect of Sulfate.—The explanation of the peculiar effect of the presence of sulfate on the completeness of precipitation of zirconium selenite is probably analogous to that proposed by Ruer in his studies on the precipitation of zirconium oxalate.[7] Ruer found that the addition of oxalate to zirconyl chloride solution gave a precipitate, but the addition of oxalate to zirconyl sulfate solution or to a mixture of zirconyl chloride and alkali sulfate gave no precipitate. He assumed the ionization of zirconyl sulfate to be

$$ZrOSO_4{\cdot}H_2SO_4 \longrightarrow [ZrOSO_4{\cdot}SO_4]^{=} + 2H^+$$

This assumption is borne out by the experimental fact that upon electrolysis of zirconyl sulfate the zirconium migrates to the anode, whereas with zirconyl chloride the zirconium migrates to the cathode.

Applying the same theory to the precipitation of zirconium selenite from sulfate solution, the following equilibria may be written

$$\begin{array}{lcl} [ZrOSO_4{\cdot}SO_4]H_2 & \rightleftharpoons & ZrO^{++} + 2SO_4^{=} + 2H^+ \\ ZrO^{++} + H_2SeO_3 & & ZrOSeO_3 + 2H^+ \\ ZrOSeO_3 + H_2SeO_3 & & Zr(SeO_3)_2 + H_2O \end{array}$$

Application of the principle of mass action to these equilibria shows that an increase in acidity and in sulfate-ion concentration would cause a decrease in solubility of the selenite precipitate. This is borne out by the experimental data. It is likewise apparent that a considerable excess of precipitating agent is desirable.

Metals Precipitated by Selenious Acid.—Solutions of various metal ions were treated individually with selenious acid solution to determine those precipitated by that reagent. In each case, 10 mg. of metal was present in 25 cc. of solution which was also 0.6 N in hydrochloric acid (except that 0.6 N nitric acid was used where an insoluble chloride could be formed). All the common cations were tested for, as well as various members of the rare earth group and of the gold and platinum groups. Thallium, beryllium, molybdenum, vanadium, tungsten, and uranium were also included.

The only elements which precipitated with selenious acid from the acid

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[7] R. Ruer, Z. *anorg. Chem.*, **42**, 87 (1904).

solution were zirconium, titanium, thorium and ceric cerium. (Ferrous iron and stannous salts precipitated free selenium by reduction of the reagent.)

Although Berg and Teitelbaum[8] have shown that bismuth precipitates quantitatively with selenious acid from solutions which are 0.25–0.33 N in nitric acid, bismuth does not precipitate from this concentration of hydrochloric acid nor from solutions which are 0.60 N in hydrochloric or nitric acid, the latter concentration being the one used in the finally adopted method for zirconium. Ferric iron, silver and mercuric mercury also form insoluble selenites but these are likewise soluble in 0.60 N acid.[9]

Although no experimental evidence has been obtained, the element hafnium undoubtedly behaves like zirconium in its reaction with selenious acid, and if present in the original sample would not be distinguished from zirconium by this method. This is, of course, equally true of all other methods in common use.

Elimination of the Effect of Titanium and Cerium.—Smith and James have claimed that the presence of hydrogen peroxide prevents the precipitation of titanium by selenious acid. Since hydrogen peroxide in acid solution also reduces ceric cerium to the cerous form, which is unprecipitated by selenious acid, it would seem that hydrogen peroxide could be used to cause precipitation of pure zirconium selenite by selenious acid even in the presence of titanium and cerium. Twenty-five cc. portions of the standard zirconyl chloride solution were mixed with solutions of ceric nitrate and titanium chloride, 20 cc. of hydrogen peroxide and 20 cc. of 6 N hydrochloric acid were added. The solutions were heated and diluted to 400 cc. and the zirconium precipitated with 20 cc. of 10% selenious acid. The results were as follows.

ZrO_2 present, g.	Ce^{++++} added, g.	Ti^{++++} added, g.	ZrO_2 found, g.
0.1200	0.050	...	0.1201
.1200	.050	...	.1195
.1200	...	0.050	.1338
.1200	.050	.050	.1341
.1200	.050	.050	.1331

This would indicate that zirconium selenite can be precipitated pure in the presence of cerium if hydrogen peroxide has been added to reduce the cerium to the trivalent state but that zirconium cannot be precipitated pure by one precipitation in the presence of much titanium even in the presence of hydrogen peroxide. Since basic zirconium selenite, if freshly precipitated, can be dissolved in hot 6 N hydrochloric acid, the above

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[8] R. Berg and M. Teitelbaum, *Z. anorg. allgem. Chem.*, *189*, 101 (1930).

[9] Mercurous mercury precipitates with selenious acid, even from 0.6 *N* nitric acid solution, but in the adopted procedure the preparation of the solution would bring about oxidation of any mercurous mercury.

determinations were repeated, but the zirconium precipitates were washed by rough decantation, dissolved in hot 6 *N* hydrochloric acid, and the zirconium reprecipitated under the same conditions as above. The results were as follows.

ZrO_2 present, g.	Ce^{++++} added, g.	Ti^{++++} added, g.	ZrO_2 found, g.
0.1200	...	0.050	0.1203
.1200	...	.050	.1211
.1200	0.050	.050	.1207
.1200	.050	.050	.1205

Double precipitation by selenious acid in the presence of hydrogen peroxide therefore suffices to precipitate zirconium nearly completely, uncontaminated by cerium or titanium.

Elimination of the Effect of Thorium.—The presence of the element thorium gives greater difficulty in the determination of zirconium by selenious acid, since it is precipitated by the reagent and is not affected by hydrogen peroxide. Smith and James dismissed this difficulty with the statement that thorium is rarely present in zirconium ores, but Dana[10] lists many zirconium ores in which thorium is present in considerable amount.

The two most common methods of separating thorium from zirconium are with hydrofluoric acid and with oxalic acid. Since the former method requires platinum ware and other special forms of apparatus, it was not experimentally applied to this case. Oxalic acid precipitates thorium oxalate from slightly acid solution and leaves zirconium in solution. Since, however, zirconium selenite will not precipitate from solutions containing oxalate, it becomes necessary in this case to remove excess oxalate after filtering off the thorium precipitate. An attempt was first made to destroy this oxalate with concentrated permanganate solution, but, besides introducing a very large amount of manganese into the solution, it was found difficult to destroy all of the oxalate by this method. It seemed best to destroy oxalate by evaporation with sulfuric acid, but since all but a small amount of sulfate must be absent from the solution from which zirconium is precipitated, an additional step is necessary, namely, that of precipitating zirconium with ammonium hydroxide and dissolving in hydrochloric acid before precipitating with selenious acid.

In the following determinations, zirconium (+thorium) was first precipitated with selenious acid from 0.6 N hydrochloric acid solution, the precipitate was dissolved in hot 6 N hydrochloric acid and 40 ce. of hot 10% oxalic acid solution. The solution was diluted to 200 cc. with hot water and made 0.36 N in hydrochloric acid. After standing overnight, the thorium oxalate was filtered off and the filtrate evaporated with 18 N

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[10] E. S. Dana, "System of Mineralogy."

sulfuric acid until oxalate was completely destroyed. The solution was diluted and made ammoniacal. The precipitate was filtered, washed superficially with water and dissolved in 15 cc. of hot 12 *N* hydrochloric acid. The solution was then treated with 20 cc. of 3% hydrogen peroxide, diluted to 400 cc. and the zirconium was precipitated from the hot solution with selenious acid. The results were as follows.

ZrO_2 present, g.	Th^{++++} added, g.	ZrO_2 found, g.
0.1200	0.050	0.1190
.1200	.050	.1195
.1200	.050	.1191
.1200	.050	.1178

The somewhat low values seemed to indicate the probability of some zirconium precipitating with the thorium. Scott[11] recognizes this possibility and recommends two precipitations of thorium in its separation from zirconium. In the next series of determinations this was done by decomposing the precipitated thorium oxalate by evaporation with 18 *N* sulfuric acid. The solution was diluted, made just ammoniacal and then slightly acid. The thorium was again precipitated with oxalic acid and the filtrates were united before proceeding as above with the precipitation of the zirconium. Erratic results were obtained for the weights of zirconium dioxide, however, some being within 0.3 mg. of the correct value (*i.e.*, 0.1200 g.) while others ran as high as 0.1315 g. It seemed obvious, therefore, that thorium oxalate is incompletely precipitated in the presence of a large concentration of sulfate ion. This was substantiated by a series of determinations in which the thorium in 25-cc. portions of thorium nitrate solution was precipitated with 10% oxalic acid solution from 0.36 N hydrochloric acid solution in the presence of varying amounts of sulfate The thorium oxalate precipitates were ignited to oxide and the results were as follows.

(Gram ThO_2 present = 0.1660)

Gram-equivalents of sulfate present	0.090	0.180	0.360	0.540
G. ThO_2 obtained, g.	.1658	.1656	.1581	.1524

This effect of high sulfate concentrations in preventing the complete precipitation of thorium oxalate is therefore analogous to the effect of sulfate on the precipitation of zirconium oxalate as studied by Ruer. It also explains the erratic results obtained in the above determinations of zirconium when thorium was precipitated twice, for somewhat variable amounts of sulfate were present in the second precipitation of thorium. The obvious remedy for this error is to precipitate the thorium with ammonium hydroxide, after reprecipitating with oxalic acid. This addi-

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[11] W. W. Scott, "Standard Methods of Chemical Analysis," 4th ed., p. 622.

tional step was therefore included in the method finally adopted and described below.

Experiments on Adsorption.—Since freshly precipitated zirconium selenite can be redissolved in hot 6 *N* hydrochloric acid and reprecipitated from the diluted solution, and since the final proposed method involves three such precipitations, it was felt that any possibility of error due to adsorption of foreign elements would be eliminated. The following experiments were made, however, to verify this conclusion.

The zirconium in 25-cc. portions of the standard zirconyl chloride solution (equivalent to 0.1200 g. of ZrO_2) was precipitated from 400 cc. of solution containing 40 cc. of 6 *N* hydrochloric acid and 0.20 g. of various metal ions. It was found that even with a single precipitation of zirconium the elements manganese, zinc, cobalt, copper, lead, bismuth, iron, aluminum, and rare earth metals are not seriously adsorbed, the maximum adsorption increasing the weight of ZrO_2 obtained to 0.1210 *g*. With two precipitations, the adsorption in each case was negligible, being not greater than 0.2 mg. Uranyl ions were considerably brought down by one precipitation (ZrO_2 found, 0.1225 g.) but not by two precipitations (ZrO_2 found, 0.1202 *g.*). Vanadium as vanadate was greatly adsorbed (0.1415 g. ZrO_2) but on dissolving the precipitate in hot hydrochloric acid, vanadate is reduced to vanadyl ions, which are not brought down by zirconium selenite, and 0.1200 g. of ZrO_2 was obtained. Since in the proposed method hydrogen peroxide is to be added to hold cerium and titanium in solution, any vanadium would be converted to pervanadic acid. Pervanadic acid, like vanadate, is greatly adsorbed by zirconium selenite (in the presence of 0.20 g. of vanadium as pervanadate 0.1294 g. of ZrO_2 was obtained), so in the proposed method of analysis one precipitation of zirconium selenite is made without the addition of hydrogen peroxide and following the addition of alcohol to reduce any vanadate to the vanadyl form.

Proposed Methods of Analysis

Proposed Method for Zirconium when Present in Solution.—To the nearly neutral solution, which should be free from phosphate, sulfate, columbium and tantalum and which should have a volume not much greater than 100 cc., add 20 cc. of 12 N hydrochloric acid and 20 cc. of alcohol. Heat nearly to boiling, dilute to 500 cc., again heat to boiling and add 20 cc. of 10% selenious acid solution. Allow to stand hot until the supernatant liquid is clear enough to filter (preferably not over two hours). Filter and wash superficially with hot water. Puncture the paper and thoroughly flush off the precipitate into the original beaker with a fine stream of hot water, using as little as possible and saving the paper. Add 15 cc. of 12 *N* hydrochloric acid and heat until the precipitate is dissolved (a slight turbidity sometimes persists but may be permitted to remain). Add 20 cc. of 3% hydrogen peroxide, warm, dilute to 500 cc., heat to boiling, and again precipitate with 20 cc. of 10% selenious acid. Filter and wash with hot water. Again puncture the paper and flush off the precipitate.

(A) In a small beaker digest the two filter paper.: with 40 cc. of hot 10% oxalic acid solution. Filter and wash the pulp, and add the filtrate and washings to the zirconium precipitate. Dilute to **200** cc., heat to boiling and add **12** cc. of **6** N hydrochloric acid. Let stand at room temperature for at least ten hours. Filter and wash the precipitate with a solution containing **40** cc. of **6** N hydrochloric acid and **25** g. of oxalic acid per liter. To the filtrate add **30** cc. of **18** N sulfuric acid and start evaporating on the water-bath, covering the beaker with a large watch-glass supported on a glass triangle. (If the oxalate precipitate is large, flush it off into a 400-cc. beaker, add **5** cc. of **18** N sulfuric acid and evaporate on the water-bath until oxalate has been destroyed, as shown by the cessation of the evolution of gas bubbles. Dilute with water, make ammoniacal, filter and dissolve in **12** cc. of **6** N hydrochloric acid. Dilute to **160** cc., heat to boiling, and add **40** cc. of 10% oxalic acid. Let stand for at least ten hours and filter into the main solution.) Evaporate on the water-bath until oxalate has been destroyed as shown by the cessation of the evolution of gas bubbles. Wash down the sides of the beaker and watch-glass and filter any precipitated selenium. If a small amount of red selenium runs through the paper it may be neglected. Make the solution ammoniacal, filter and wash superficially with hot water. Puncture the paper and flush off the precipitate with as little hot water as possible. Pour **15** cc. of hot **12** *N* hydrochloric acid over the paper into the zirconium hydroxide suspension and heat until the precipitate is entirely dissolved. (B)

Add **20** cc. of **3%** hydrogen peroxide and warm. Dilute to **500** cc. and heat to boiling. Add **20** cc. of **10%** selenious acid and filter after the supernatant liquid is clear. Ignite over the Bunsen flame and finally for five minutes over the Méker burner. Weigh as ZrO_2.

In the known absence of thorium, the above method may be shortened. The oxalate precipitation involved in the above directions from (A) to (B) may be omitted. In this case, dissolve the zirconium selenite precipitate obtained at (A) by adding **20** cc. of **12** N hydrochloric acid and heating to boiling. Continue from point (B). Ignite the two filter papers from which the first two precipitates were washed and add the weight of their ash to the final weight of ZrO_2.

Results Obtained by Use of the Proposed Method.—The above proposed method for the determination of zirconium was applied to the following mixtures and the values obtained are shown in the last column. It may be pointed out that the mixtures used are such as to offer greater difficulty than would be encountered in an ordinary analysis.

ZrO_2 present, g.	Th^{++++}, g.	Ce^{++++}, g.	Ti^{++++}, g.	V as VO_3^-, g.	U as UO_2^{++}, g.	Fe^{+++}, g.	ZrO_2 found, g.
0.1200	**0.050**	**0.050**	**0.050**	...	..	..	**0.1202**
.1200	.050	.030	.040	**0.040**	**0.050**	**0.050**	.1198
.1200	.050	.030	.040	.040	.050	.050	.1201
.1200	.050	,030	.040	.040	.050	.050	.1189

Decomposition of Zirconium Ores.—The most satisfactory methods for the decomposition of zirconium minerals are fusion with sodium peroxide or sodium peroxide mixtures, fusion with borax, and fusion with alkali fluorides. Of these, a strong alkaline fusion should serve best in cases where zirconium is subsequently to be determined by the selenite method, for by this fusion the interfering constituents phosphate, columbium and tantalum can be removed most easily. Hillebrand and Lundell[12] state that

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[12] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Chemistry," John Wiley and Sons, Inc., New York, p. **445.**

phosphate is best removed by fusion of the original material with sodium peroxide and leaching with water. Some columbium and tantalum are removed in this way, but by fusing the residue with potassium carbonate or potassium hydroxide, columbium and tantalum can be practically completely removed. Schoeller and Powell[13] have studied this separation and have worked out a procedure which, according to Hillebrand and Lundell, serves as probably the best method for the removal of these elements. In this connection the authors state that it is preferable to dissolve in acid the extraction residue from the first fusion, precipitate with ammonia and use the ignited precipitate for the second fusion rather than to fuse the residue directly.

Fusion with sodium peroxide is usually carried out in a nickel crucible and for ordinary zirconium ores requires about twenty minutes. A simple procedure for sodium peroxide fusions and one that is complete in a very short time is that devised by Muehlberg.[14] This consists in mixing the sample with sugar carbon and sodium peroxide and igniting, the crucible being kept covered and also immersed in running water during the ignition and subsequent cooling. The melt shrinks when cooling and can be easily removed from the crucible. It has the very great advantage of introducing no nickel from the crucible into the melt. The method has been further studied by Marvin and Schumb,[15] who have determined the exact conditions for the most satisfactory decomposition of refractory substances and have found that all common refractories yield to the treatment, including zircon and other zirconium ores.

The following directions serve as a rapid method not only for decomposing zirconium ores but also for removing phosphate, columbium and tantalum. The method prepares the material for the determination of the zirconium by the selenite method given above.

Proposed Method of Attack of Zirconium Ores.—Place in a 50-cc. nickel crucible about 25 g. of an intimate mixture (made by gently rolling the two constituents in a large dry bottle) of 15 parts of fine sodium peroxide with 1 part of 100-mesh pure sugar carbon. Weigh out 1 g. of the finely ground sample upon this mixture, cover with more fusion mixture and mix intimately at the surface with a spatula. Cover with a liberal layer of the fusion mixture and immerse in cold running water so that the level of the water is slightly above the level of the contents of the crucible. Cautiously start the ignition by means of the glowing tip of a piece of cotton twine and immediately cover the crucible. After fusion is complete and the crucible is cold, remove the contents to a 1-liter beaker, add 300 cc. of cold water, flush out the crucible and wash off the cover. Heat nearly to boiling until the melt has disintegrated, dilute to 900 cc. with hot water, and heat until the supernatant liquid is clear enough to filter. Filter and wash the residue with hot water. Reject the filtrate. (If much phosphate is present or if columbium or tantalum is present in small amounts, treat the residue with hydrochloric acid and without filtering

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[13] W. R. Schoeller and A. R. Powell, J. Chem. *Soc.*, 119, 1928 (1921).

[14] W. F. Muehlberg. *Ind. Eng. Chem.*, 17, 690 (1925).

[15] G. G. Marvin with W. C. Schumb, THIS JOURNAL, 52, 574 (1930).

add excess ammonia. Filter, ignite the residue and repeat the fusion and leaching as above.) Dissolve the residue in hydrochloric acid and filter off any undissolved material. This is essentially carbon but it may contain a very small amount of undecomposed original material (seldom more than one milligram), which can be separately fused with sodium peroxide–carbon mixture and the residue, after leaching with water, dissolved in hydrochloric acid and added to the main solution. To the hydrochloric acid solution add 25 cc of 18 N sulfuric acid and evaporate to fuming. Cool, dilute with water and filter off any silica. Make the filtrate ammoniacal, filter, wash superficially with hot water and dissolve in 15 cc of 12 N hydrochloric acid. The solution is then ready for the determination of zirconium by the method described above.

With moderate or high percentages of columbium or tantalum, treat the residue from the first peroxide–carbon fusion with hydrochloric acid and without filtering add excess ammonia. Filter and wash superficially with hot water. Ignite and fuse for five minutes in a platinum crucible with 20 parts of potassium carbonate. Leach with hot water, filter, and wash with 2% potassium carbonate solution and then with hot water. With high percentages of columbium and especially with high percentages of tantalum fuse the residue again with potassium carbonate. Leach with water; ignite the residue and fuse in the original platinum crucible with potassium pyrosulfate. Extract with 200 cc. of hot water, containing 10 cc. of 18 N sulfuric acid, filter, make the solution ammoniacal, filter and wash superficially with hot water. Dissolve the precipitate in 15 cc. of 12 N hydrochloric acid. The solution is then ready for the precipitation of zirconium as described above.

Results Obtained by the Proposed Fusion Method.—Artificial ores, made by mixing pure ZrO_2 with feldspar, apatite, and Cb_2O_5, when fused according to the directions above and the zirconium precipitated with selenious acid, gave the following values.

ZrO_2, g.	0.0837	0.0973	0.1112	0.1183	0.1091	0.1034
Feldspar,[a] g.	.66	.60	.50	.30	.50	.30
Apatite (=32% P_2O_5),[a] g.	.13	.14	.12	.050	.050	.050
Cb_2O_5,[a] g.	....	....	....	.050	.050	.050
Sample, g.	.8705	.8340	.7280	.5201	.7132	.5052
ZrO_2 found, g.	.0830	.0950	.1109	.1184	.1100	.1040
% ZrO_2 present	9.62	11.66	15.28	22.75	15.30	20.46
% ZrO_2 found	9.54	11.39	15.23	22.77	15.43	20.58

[a] Approximate weights only, as indicated.

Summary

1. Zirconium is quantitatively precipitated as basic selenite by excess selenious acid from solutions the acidity of which should not be greater than 0.6 *N*.

2. Hydrochloric acid is the best acid medium for this precipitation. Sulfuric acid causes a much slower precipitation, presumably of the crystalline normal selenite, and the precipitate is more difficult to remove from the beaker and more difficult to redissolve.

3. The presence of more than a small amount of sulfate prevents quantitative precipitation of zirconium from hydrochloric acid or sulfuric

acid solution. Increasing sulfate requires decreasing acidity for quantitative precipitation. This effect is probably due to the formation of $[ZrOSO_4 \cdot SO_4]H_2$, which provides few zirconium or zirconyl ions.

4. The elements zirconium (with hafnium), titanium, thorium and ceric cerium are the only dements which can ordinarily be present in a zirconium mineral which are precipitated either wholly or in part by selenious acid from 0.6 N hydrochloric acid solution.

5. The precipitate of zirconium basic selenite, if not allowed to stand suspended in hot solution long enough to become crystalline, can be redissolved in hot 6 N hydrochloric acid and therefore can be reprecipitated free from adsorbed elements (*e.* g., vanadate and uranyl salts which are considerably brought down by the zirconium precipitate). Vanadium, if previously reduced to vanadyl salt, is not brought down by the zirconium precipitate.

6. The addition of hydrogen peroxide before the precipitation of zirconium causes reduction of ceric cerium, therefore prevents its precipitation, and holds up titanium sufficiently so that it is eliminated by two precipitations of zirconium selenite.

7. Quantitative separation of thorium can be effected by double precipitation of thorium oxalate in the absence of sulfate and subsequent removal of excess oxalate by evaporation with sulfuric acid.

8. A method for the analysis of zirconium by means of selenious acid is given in detail. This gives satisfactory results even when all of such elements as thorium, ceric cerium, titanium, vanadium, iron and uranium are originally present.

9. A rapid method for decomposing zirconium ores preparatory to making the above analysis is also given. By this method phosphate, columbium and tantalum can be eliminated and the selenite method as given then serves as a satisfactory method for zirconium in any zirconium ore.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

TERNARY SYSTEMS. IX. SODIUM IODATE, SODIUM NITRATE AND WATER[1]

BY ARTHUR E. HILL AND JOHN E. DONOVAN

RECEIVED DECEMBER 19, 1930 PUBLISHED MARCH 6, 1931

In the Caliche from which Chile saltpeter is extracted there are present a number of salt-forming ions. Of the many poly-component systems which these may compose with water a number have been investigated but a very large number still remain without published investigation. A short time ago it was decided to investigate some of these three-component and four-component systems at New York University. During the process of this work, there appeared the investigations by Foote and Vance,[2] covering the system sodium iodate, sodium nitrate and water at various temperatures between the ternary eutectic and 35°. Our own work on this system, nearly completed before Foote and Vance's became known to us, contains certain isotherms at temperatures slightly different from those selected by Foote and Vance, and at a duplicate temperature in the case of the 25° isotherm. Our findings are in general accord with those of the earlier publication; the two sets of investigations gave a rather unusually complete set of data for a ternary system. To the earlier isotherms at 0, 8, 25 and 35° we add as new material the isotherms at 5 and at 50°.

Attainment of Equilibrium.—The solubility data on sodium iodate and water, previous to the work of Foote and Vance,[2] were both discordant and misleading, because of confusion as to the degree of hydration of the saturating salt (seven hydrates having been mentioned by various authors[3]) and also doubtless because of difficulties, which we shall point out, in the attainment of equilibrium. The stable hydrates found by us are in agreement with the findings of Foote and Vance, namely, $NaIO_5 \cdot 5H_2O$ below 20°, $NaIO_3 \cdot H_2O$ between 20 and 70°, above which temperature the anhydrous salt is stable in contact with solution. In the matter of attainment of equilibrium we have found the various alkali and alkaline-earth iodates to be extremely slow, as will be pointed out in later publications relative to the magnesium and potassium salts; and where in addition the formation of a hydrate is involved, as in the case of the sodium salt, the quantitative change to that form is also slow, giving most annoying retardation in the attainment of both internal and external equilibrium. We have given some considerable study to this problem and are in possession of the facts even though no remedy has been found outside of an extremely lengthy

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[1] The material of this paper was presented by John E. Donovan in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Foote and Vance, *Am. J. Sci.*, 16, 68 (1928); 18,375 (1929).

[3] See Mellor, "Comprehensive Treatise," Vol. II, p. 334.

agitation of the salt with water. The first very important finding is that if experiments are made with use of the anhydrous salt at any temperature at which a hydrate is the stable form, the equilibrium can be approached only from the side of supersaturation; samples treated with cold water and agitated at 25° showed a solubility of the order of 8.79% at the end of three hours, dropping slowly thereafter and remaining for many days above what we believe to be the true solubility for the hydrate. This behavior is undoubtedly owing to the higher solubility of the metastable anhydrous form, and to the fact that with samples of whatever amounts of solid phase were used, the process of solution was much more rapid than the process of hydration. In the endeavor to eliminate this source of error special experiments were conducted with the purpose of providing only pure hydrate as initial solid phase. It was found, however, that samples of supposed hydrate prepared by ordinary recrystallization in the neighborhood of 25° would regularly show the same phenomenon of forming supersaturated solutions, which may be again attributed to the presence of sufficient unhydrated salt to give the high results. It was only after a sample of the supposed hydrate had been agitated with new solvent three times and for a period of about two weeks at each treatment that it could be made to give results which could not be regarded as an approach from supersaturation. The elimination of this source of error, however, did not help with the second, which is the slow attainment of equilibrium. In only one instance have we been able to secure results, from true supersaturation and true undersaturation, which were within the limits of our analytical error, which for the determination of iodate by iodimetry we place at 0.2% as an extreme, and which probably is nearer 0.1%. The following results in Table I are typical.

TABLE I

$NaIO_3 + H_2O$ AT 25° (SOLID, $NaIO_3 + H_2O$)

Time	From undersaturation, %	From supersaturation, %	Difference in, %
3.5 hours	8.561	8.829	3.1
1 day	8 576	8.703	1.5
4 days	8.568	8.694	1.24
11 days	8.560	8.680	1.39
23 days	8.564	8 665	1.21

The two samples have remained more than 1% apart in solubility after twenty-three days, and show no marked trend after the fourth day. Similar results have been found in this Laboratory by Professor S. F. Brown and Mr. J. E. Ricci, in the course of investigations to be reported later. In one instance the solubility approached from supersaturation came down to 8.56% in thirty-five days; we therefore conclude that the figures from undersaturation, obtained after any briefer interval, are more nearly correct than those approached from supersaturation. We are quite unable to agree with Foote and Vance that equilibrium from both directions has been reached, within narrow limits, in four to six hours, and raise the question as to whether their agreement between results from undersaturation and supersaturation at this temperature (8.65 and 8.66%) and at other temperatures may not be due to the use of anhydrous salt and the consequent agreement of two samples both from supersaturation. As a practical experimental matter, however, we have used the anhydrous salt as our original solid (this being necessary for our calculations in the ternary system) and have allowed a time of rotation from one week to two weeks; there is no evidence that longer periods, within reasonable limits, would add materially to the accuracy.

The Binary System, Sodium Iodate–Water.—For this work recrystallized and dehydrated salt in generous amount was put in 40-cc. glass-stoppered pyrex test-tubes and rotated in a water thermostat, constant to within 0.05°, for periods of about two weeks. The results are therefore those obtained from supersaturation, and are given in Table II.

TABLE II

SOLUBILITY OF $NaIO_3$ IN WATER

Temp., °C.	Wt. % of $NaIO_3$	Density of solution	Solid phase
5	3.30	1.028	$NaIO_3 \cdot 5H_2O$
15	5.85	1.051	$NaIO_3 \cdot 5H_2O$
20	7.81	...	$NaIO_3 \cdot H_2O + NaIO_3 \cdot 5H_2O$
22	8.11	1.071	$NaIO_3 \cdot H_2O$
25	8.67	1.077	$NaIO_3 \cdot H_2O$
35	10.58	1.093	$NaIO_3 \cdot H_2O$
40	11.70	...	$NaIO_3 \cdot H_2O$
50	13.95	...	$NaIO_3 \cdot H_2O$

These solubility data agree with those of Foote and Vance within 0.01 to 0.03% up to 40°, leading us to believe that their experiments were also done with the anhydrous salt and therefore represent approach to equilibrium from supersaturation. The densities are approximate figures, obtained by weighing the solution delivered by a calibrated 5-cc. pipet. The intersection of the two solubility curves, shown in Fig. 1, is at 20° within the accuracy of our measurements; this also is in accord with Foote and Vance's figure of 20.3° obtained by careful calculation from the logarithmic curves for the solubility against the inverse of the absolute temperature; their results by the thermal and dilatometric methods are about 0.5° lower. The composition of the hydrate stable at room temperature was determined by analysis for water content after samples slowly formed by isothermal evaporation had been brought to constant weight over the anhydrous form as desiccating agent in miniature desiccators; it gave 8.31% H_2O, 8.34% being required by the formula $NaIO_3 \cdot H_2O$. Difficulties in maintaining desiccators at the lower temperatures for the pentahydrate were such that the crystallized salt was simply centrifuged well and analyzed directly.; samples gave from 32.17 to 32.52% water, where 31.28% is required by the formula $NaIO_3{\cdot}5H_2O$. We confirm the findings of Foote and Vance that these are the only stable hydrates found in the temperature range studied, and that Meerburg's[4] formula $NaIO_3{\cdot}{}^3/_2H_2O$ is not valid.

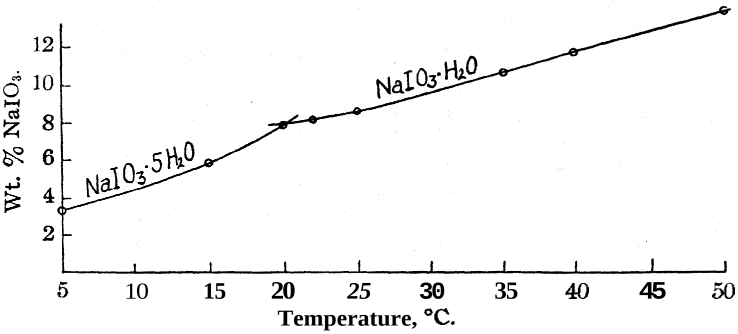

Fig. 1.—Solubility of sodium iodate in water.

The Ternary System.—For the study of the ternary system, good grades of sodium nitrate and sodium iodate were purified by crystallization. Weighed quantities of these salts were treated with weighed amounts of water in pyrex test-tubes and vigorously shaken by hand to prevent caking of the hydrate formed. The tubes were then slowly rotated in a water thermostat at the desired temperature for periods of about two weeks. After the tubes had been allowed to settle, samples were withdrawn into a calibrated pipet fitted with a small filter of absorbent cotton. One sample was weighed and evaporated in a platinum dish to constant weight at 110°, about twenty-four hours being required. From this the water content of the saturated solution became known. A second weighed sample was treated with potassium iodide and sulfuric acid and titrated with sodium thiosulfate solution, previously standardized against pure potassium iodate. The content of sodium iodate being thus established, the sodium nitrate was obtained by subtraction. The data at three temperatures are given in Table III, and plotted in Figs. 2, 3 and 4.

Since data were at hand both for the composition of the phase complex used and for the saturated solution, it was possible to extrapolate graphically or algebraically the line connecting these two points and thus determine approximately the composition of the solid phase, whenever it was a two-component body, by the intersection of this line with the side of the triangle. It was this procedure which first made clear to us, in the study of the 25° isotherm, that the solid phase is a monohydrate and not the more complex hydrate suggested by Meerburg. Following this method, two

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[4] Meerburg, *Z. anorg. Chem.*, 45, 324 (1905).

TABLE III

THE SYSTEM: $NaIO_3$–$NaNO_3$–H_2O

Temp., °C.	Point in diagram	Original Complex Wt, % of $NaIO_3$	Original Complex Wt, % of $NaNO_3$	Saturated Solution Wt, % of $NaIO_3$	Saturated Solution Wt, % of $NaNO_3$	Density	Solid phase
	k	9.00	0.00	3.30	0.00	1.028	$NaIO_3 \cdot 5H_2O$
		9.02	4.00	1.58	4.50	1.042	$NaIO_3 \cdot 5H_2O$
		9.03	20.07	1.55	22.59	1.182	$NaIO_3 \cdot 5H_2O$
		10.05	23.11	1.65	26.38	1.214	$NaIO_3 \cdot 5H_2O$
		12.07	24.12	1.75	28.44	1.230	$NaIO_3 \cdot 5H_2O$
		10.03	27.08	1.87	30.70	1.255	$NaIO_3 \cdot 5H_2O$
		12.02	26.64	1.78	31.38	1.262	$NaIO_3 \cdot 5H_2O$
		12.04	28.09	2.10	31.54	1.263	$NaIO_3 \cdot 5H_2O$
		8.99	29.94	2.07	32.48	1.275	$NaIO_3 \cdot 5H_2O$
		12.02	27.54	1.86	32.37	1.269	$NaIO_3 \cdot 5H_2O$
5	f	...	...	1.94	34.34	1.291	$NaIO_3 \cdot 5H_2O$ + compound
		9.02	35.07	1.76	36.69	1.308	Compound
		12.02	35.55	1.60	38.38	1.324	Compound
		9.01	27.04	1.52	39.17	1.331	Compound
		9.03	38.11	1.41	40.40	1.336	Compound
	c	...	...	1.28	42.74	1.359	Compound + $NaNO_3$
		1.00	50.11	1.01	42.94	1.359	$NaNO_3$
	a	0.00	55.00	0.00	43.42	1.368	$NaNO_3$
	f	15.00	0.00	8.67	0.00	1.077	$NaIO_3 \cdot H_2O$
		9.60	2.89	6.38	3.26	1.078	$NaIO_3 \cdot H_2O$
		11.35	3.69	5.99	3.91	1.078	$NaIO_3 \cdot H_2O$
		9.01	7.01	4.80	7.32	1.092	$NaIO_3 \cdot H_2O$
		6.00	10.01	4.30	10.10	1.109	$NaIO_3 \cdot H_2O$
		4.00	16.01	3.68	16.08	1.149	$NaIO_3 \cdot H_2O$
25		9.10	18.19	3.41	19.47	1.171	$NaIO_3 \cdot H_2O$
		10.01	25.02	3.06	27.16	1.232	$NaIO_3 \cdot H_2O$
		10.01	30.02	2.84	32.67	1.276	$NaIO_3 \cdot H_2O$
		10.00	35.01	2.60	38.19	1.328	$NaIO_3 \cdot H_2O$
		10.04	41.15	2.31	45.12	1.392	$NaIO_3 \cdot H_2O$
	c	...	...	2.23	46.81	1.408	$NaIO_3 \cdot H_2O$ + $NaNO_3$
		0.92	55.36	1.09	47.44	1.396	$NaNO_3$
	a	.00	55.00	0.00	47.98	1.388	$NaNO_3$
	h	20.00	0.00	13.95	0.00		$NaIO_3 \cdot H_2O$
		19.05	5.02	9.63	5.74		$NaIO_3 \cdot H_2O$
		16.02	15.02	6.22	17.03		$NaIO_3 \cdot H_2O$
		14.08	25.14	4.82	28.18		$NaIO_3 \cdot H_2O$
		13.01	35.01	3.92	39.15		$NaIO_3 \cdot H_2O$
		12.99	35.97	4.00	39.94		$NaIO_3 \cdot H_2O$
50	f	...	...	3.84	41.53		$NaIO_3 \cdot H_2O$ + $NaIO_3$
		11.01	39.01	3.77	42.26		$NaIO_3$
		11.03	40.09	3.64	43.46		$NaIO_3$
		10.95	41.81	3.46	45.23		$NaIO_3$
		11.01	45.04	3.09	49.11		$NaIO_3$
	c	...	...	2.91	51.86		$NaIO_3$ + $NaNO_3$
		1.30	55.04	1.58	52.55		$NaNO_3$
	a	0.00	64.00	0.00	53.50		$NaNO_3$

points of interest were noted: first, that at 50° the anhydrous sodium iodate is solid phase in the solutions more highly concentrated with sodium nitrate, although the temperature is 20° below the transition temperature for that salt, as found by Foote and Vance; and, second, that at 5° a double salt exists, in contact with solutions of a restricted range of concentrations, as likewise reported by Foote and Vance for S°.

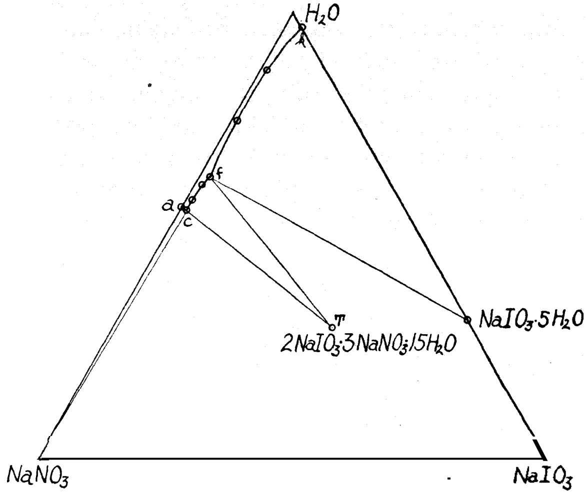

Fig. 2.—5° Isotherm: $NaIO_3$–$NaNO_3$–H_2O.

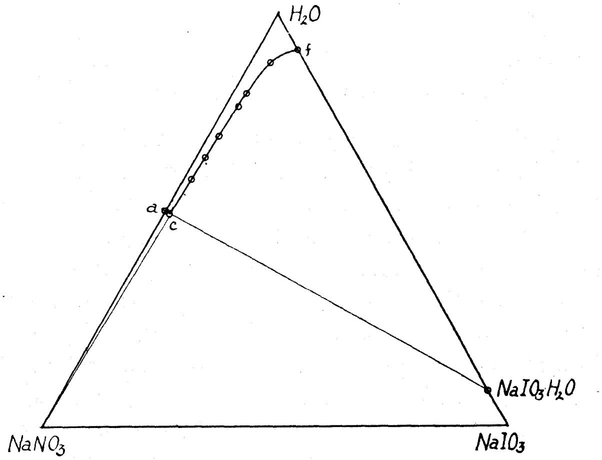

Fig. 3.—25° Isotherm: $NaIO_3$–$NaNO_3$–H_2O.

The Double Salt.—The double salt which appears in the 5° isotherm was prepared for analysis by making a complex of phases which fell within the triangle cTf of Fig. 2, bringing the solids completely into solution by warming, and then allowing the solution to cool quietly to 5° without the formation of solid phase, which was not difficult because of the marked slowness with which precipitation of the iodate (and presumably of the double salt) is known to occur. Upon agitating the tube in the thermostat, however, the first precipitation was of a flocculent character, and must have been either hydrated sodium iodate or an amorphous form of the double salt. After a few hours' stirring the precipitate changed to a well-crystallized product which settled quickly and completely. After four days of stirring the sample was removed, filtered and centrifuged in an environment not above 5°. The sample was then weighed at this temperature, put in a miniature desiccator over a second sample which had been allowed to lose about half its water, and placed in a refrigerator at 7° where it was held for forty days. The solution was also analyzed and found to represent a point on the curve cf. The matter of the analysis of an incongruently soluble ternary compound has been discussed at some length in another place;[5] the essential is that the amount of mother liquor present, which is here widely different in composition from the salt, must be known so that a correction may be applied for the salts deposited upon its drying up. In this case the amount of water of solution lost during the forty days of desiccation was 1.76% of the whole, the composition of the mother liquor 1.40% $NaIO_3$ and 57.74% $NaNO_3$. The sample was analyzed in the usual manner and the results corrected for the amount of mother liquor present; the data are given in Table IV.

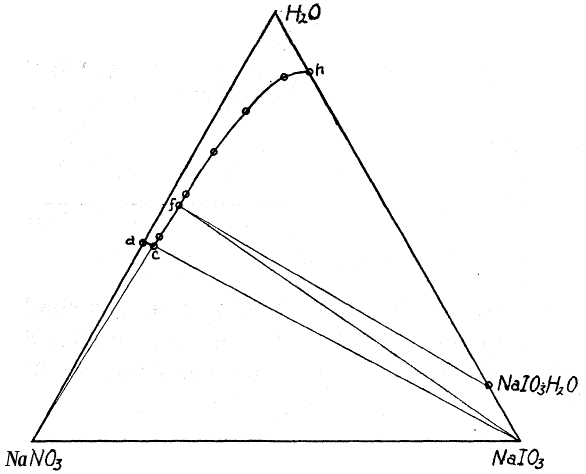

Fig. 4.—50° Isotherm: $NaIO_3$–$NaNO_3$–H_2O.

The result confirms the finding of Foote and Vance, with a somewhat better agreement between analysis and calculation.

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[5] Hill, This Journal, 52,3823 (1930).

TABLE IV

ANALYSIS OF TERNARY COMPOUND

	Uncorrected analysis, %	Corrected analysis, %	Calculated for $2NaIO_3 \cdot 3NaNO_3 \cdot 15H_2O$
$NaIO_3$	42.06	42.60	42.97
$NaNO_3$	28.91	28.00	27.69
H_2O	29.03	29.40	29.34

The upper temperature limit for the ternary compound is at about 9.6°, as found by thermal measurements—in sufficient agreement with Foote and Vance's figure 9.8°, accurate measurements not being possible because of the apparently slow formation of the compound. It is obvious that the existence of this compound will have an important influence upon the separation of sodium nitrate and sodium iodate at any temperature below this point.

Summary

1. Solubility measurements are given for sodium iodate in water between 5 and 50°, and for the three-component system consisting of sodium iodate, sodium nitrate and water at 5, 25 and 50°.
2. The stable hydrates of sodium iodate are the pentahydrate below 20°, and the monohydrate above that temperature to its transition to the anhydrous form.
3. Hydrated sodium iodate does not reach equilibrium with its solution, from both undersaturation and supersaturation, within twenty-six days or more.
4. In the ternary system below 9.8' there exists a double salt of the formula $2NaIO_3 \cdot 3NaNO_3 \cdot 15H_2O$.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORIES OF CHEMISTRY OF NEW YORK UNIVERSITY]

TERNARY SYSTEMS. X. MAGNESIUM IODATE, MAGNESIUM NITRATE AND WATER[1]

BY ARTHUR E. HILL AND SAMUEL MOSKOWITZ

RECEIVED DECEMBER 19, 1930 PUBLISHED MARCH 6, 1931

For the work upon this ternary system, knowledge of the two binary systems of a single salt and water are necessary. Investigations of the solubility of magnesium nitrate in water have been conducted by Chodnew,[2] Lescoeur,[3] Ditte,[4] Ordway[5] and Funk;[6] the latter determined that only

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[1] The material of this paper was presented by Samuel Moskowitz in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Chodnew, *Ann.*, **71**, 241 (1849).

[3] Lescoeur, *Ann. chim. phys.*, [7] **7**, 419 (1896).

[4] Ditte, *ibid.*, [5] **18**, 320 (1879); *Compt. rend.*, **89**, 641 (1879).

[5] Ordway, *Am. J. Sci.*, [2] **27**, 16 (1559).

[6] Funk, *Ber.*, **32**, 96 (1889); *Z. anorg. Chem.*, **20**, 395 (1899).

two hydrates have stable existence, $Mg(NO_3)_2 \cdot 9H_2O$ from —29 to −18°, and $Mg(NO_3)_2 \cdot 6H_2O$ from −18° to its congruent melting point at 90°. We have not repeated this work. For magnesium iodate and water it was found that the work of Millon,[7] Ditte[8] and Mylius and Funk[9] should omissions, for which reason the work has been repeated.

Magnesium Iodate and Water.—Magnesium iodate was prepared according to the method of Millon,[7] by neutralizing an aqueous solution of iodic acid with magnesium carbonate and evaporating the slightly acidified solution at above 40–50° for four days, which gave a copious crystallization of the tetrahydrate. The crystals were washed with water, air dried, ground and placed in a desiccator; here there developed an outstanding peculiarity of the compound. The tetrahydrate loses only an inappreciable weight of water at room temperature over sulfuric acid or phosphorus pentoxide; a sample of 220 g. lost about 1 mg. per day over concentrated sulfuric acid, and a sample of 67 g. lost about 0.6 mg. per day over phosphorus pentoxide. Samples kept in an oven at 110° lost rapidly for a few days, but could not be brought to an anhydrous condition in a month, the residual water being about 0.5% for finely ground samples and considerably larger for coarse samples. Mylius and Funk report the tetrahydrate as stable at 80°. These results at room temperature and even at the higher temperature are most striking in view of the fact, later shown, that the hydrate has a transition temperature at about 57.5" and therefore has a vapor tension at that temperature equal to that of the saturated solution, which may be calculated by Raoult's law as approximately 128 mm Either the vapor tension curve for this hydrate is astonishingly steep, or the hydrate shows a remarkable degree of metastability with regard to dehydration; we are inclined to accept the latter view as the better interpretation. Samples which had been over the desiccating agent for several weeks were analyzed by titration and found to have the composition $Mg(IO_3)_2 \cdot 4H_2O$ within the errors of titration. This material was later used in the three-component work as of constant and known composition, since efforts to prepare the anhydrous compound by oven treatment had not been successful.

For the solubility determinations, excess salt was treated with distilled water in glass-stoppered pyrex tubes; for the lower temperatures the tubes were rotated in a water thermostat, constant to about 0 03°. For temperatures above 50° the tubes were inserted in an air thermostat and stirred by means of a brass paddle on a mechanical stirrer; a mercury seal served to minimize evaporation. Filtered samples were withdrawn by calibrated pipets at the lower temperatures and weighed to give approximate figures for density; at the higher temperatures the samples were forced through a tube into a weighing bottle by air pressure, crystallization being easily avoided because of the marked metastability. At the lower temperatures, one to three days of stirring were found to give equilibrium from undersaturation, while from supersaturation long periods were needed. Seeding with a crystal of decahydrate was resorted to below 13°. Where the change from the tetrahydrate to the anhydrous form occurs, four days of stirring were required at 80° and two days at 90°; at 70° the solid phase used was anhydrous salt, obtained at the higher temperatures, equilibrium being reached within one day. Analysis of the centrifuged solid phase obtained at 90° was in good agreement with the requirements for the anhydrous form. The results are given in Table I and shown in Fig. 1.

The solubility figures were obtained by titrating with standard thiosulfate the iodine freed by action of the samples upon potassium iodide

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[7] Millon, *Ann. chim phys.*, [3] 9, 422 (1843).

[8] Ditte, *ibid.*, [6] 21, 154 (1890)

[9] Mylius and Funk, ***Ber.***, 30, 172 (1897).

Table I

Solubility of Magnesium Iodate in Water

Temp., °C.	Wt., % of $Mg(IO_3)_2$ in satd soln	Density	Solid phase	Temp., °C.	Wt., % of $Mg(IO_3)_2$ in satd. soln.	Density	Solid phase
−0.36	3.18	1.026	I_{10} + ice	40	10.51	1.090	I_4
+5	4.39	1.034	I_{10}	50	12.05	1.115	I_4
10	5.87	1.049	I_{10}	57.5	13.1	...	I_4
15	7.79	1.073	I_{10} (m)	70	15.7	...	I_4 (m)
5	6.09	1.047	I_4 (m)	90	19.6	...	I_4 (m)
10	6.68	1.060	I_4 (m)	60	13.2	...	I
15	7.29	1.065	I_4	70	13.3	...	I
25	8.55	1.075	I_4	80	13.4	...	I
35	9.83	1.086	I_4	90	13.5	...	I

solution with sulfuric acid. In the fourth column of the above table, the abbreviation I_{10} is used for the decahydrate, I_4 for the tetrahydrate, I for the anhydrous form; (m) indicates that the solid phase was metastable, by interpretation of Fig. 1. The system is, therefore, found to show the following invariant points: a eutectic at —0.36' found by the usual thermal means, a transition of the decahydrate to the tetrahydrate at **13.3'** (by interpolation), and a transition of the tetrahydrate to the anhydrous form at 57.5'. Because of the great tendency toward metastability, confirmation of these transition points by thermal means was not possible. Whether or not the remarkable behavior of the tetrahydrate is connected with the possible poly-basicity of iodic acid and the constitution of the compound as an acid salt rather than a true hydrate would be mere speculation in the absence of other data.

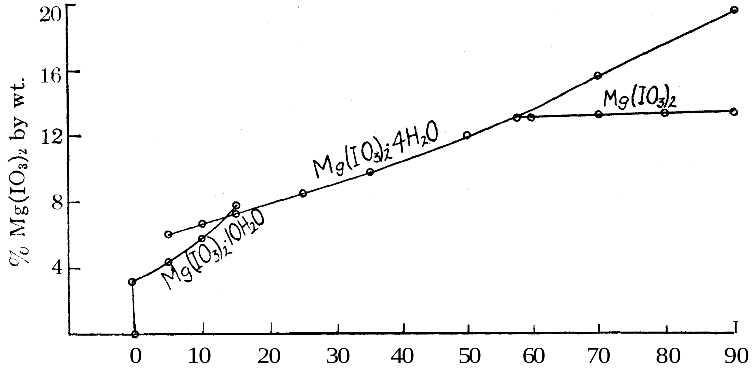

Fig. 1.—Solubility of magnesium iodate.

The Ternary System.—The phase complexes used in the study of the ternary system were made from weighed amounts of magnesium iodate tetrahydrate, water and an analyzed solution of purified magnesium nitrate nearly saturated at room temperature; the latter solution was used since it is impossible to dehydrate crystallized magnesium nitrate without hydrolytic decomposition. In a few instances it was necessary to use magnesium nitrate hexahydrate which had been partially dehydrated, in order to reduce the water content of the complex. The materials were agitated in the thermostat at the desired temperature for periods of one to three days. For the analysis of the ternary solutions, the method of iodimetry was used to give part of the necessary data, but evaporation to dryness for the water content was found impossible for the two reasons stated—incomplete dehydration of the iodate and hydrolysis of the nitrate. **A** determination of total magnesium was therefore necessary for the calculation of the composition of the solutions. Investigation of solutions

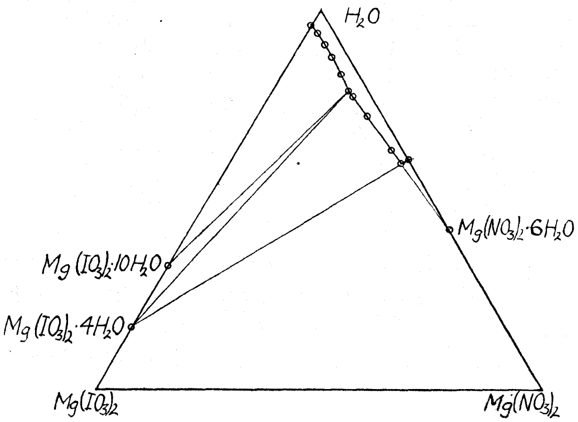

Fig. 2.—5° Isotherm: $Mg(IO_3)_2$–$Mg(NO_3)_2$–H_2O.

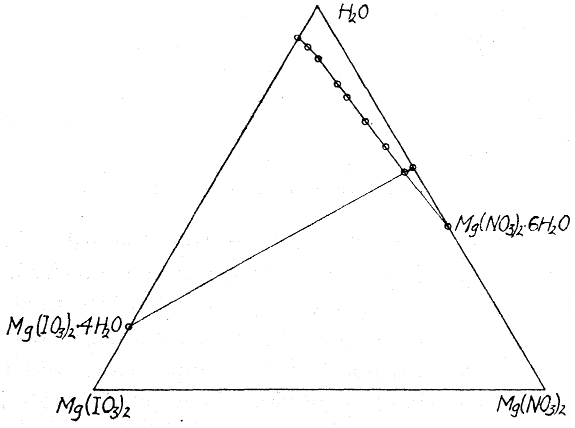

Fig. 3.—25° Isotherm: $Mg(IO_3)_2$–$Mg(NO_3)_2$–H_2O.

of known magnesium content showed that precipitation as magnesium ammonium phosphate and weighing either as the hexahydrate or by conversion to magnesium pyrophosphate gave distinctly high results; the same was true, though to a much less degree, of the values obtained by igniting the salts to form magnesium oxide. The method used, which gave results only 0.25% low with a known solution, consisted in evaporation on a steam-bath with excess sulfuric acid, finally raising the temperature over a burner to a dull red for a brief time, and weighing the residue as $MgSO_4$.

Table II gives the results obtained at 5, 25 and 50°. The curves are plotted in Figs. 2, **3** and 4.

TABLE II

SYSTEM: $Mg(NO_3)_2$–$Mg(IO_3)_2$–H_2O

Temp.	Original complex Wt., % $Mg(NO_3)_2$	Original complex Wt., % $Mg(IO_3)_2$	Saturated solution Mt., % $Mg(NO_3)_2$	Saturated solution Wt., % $Mg(IO_3)_2$	Density	Solid phase
	0.00	...	0.00	4.39	1.034	I_{10}
	2.19	11.35	2.49	3.93	1.053	I_{10}
	4.89	10.18	5.45	3.92	1.076	I_{10}
	8.03	8.96	8.86	4.03	1.105	I_{10}
	12.38	7.65	13.10	4.26	1.149	I_{10}
5°	16.43 12.22	6.77 24.39	17.00	4.55	1.184	$I_{10} + I_4$
	13.51	25.66	18.52	4.44	1.197	I_4
	17.95	24.30	24.08	3.95	1.244	I_4
	33.53	4.54	34.21	2.82	1.333	I_4
	38.36	6.69	38.10	2.39	1.368	$I_4 + N_6$
	41.48	0.40	39.02	0.46	1.352	N_6
		.00	39.25	.00	1.347	N_6
	0.0	...	0.00	8.55	1.075	I_4
	3.26	12.12	3.49	7.35	1.089	I_4
	6.91	10.91	7.31	6.66	1.116	I_4
	13.37	12.23	14.60	5.66	1.171	I_4
	17.14	10.86	18.48	5.14	1.202	I_4
25°	24.00	9.82	25.81	4.20	1.261	I_4
	29.14	13.62	33.50	3.25	1.325	I_4
		...	41.00	2.46	1.398	$I_4 + N_6$
		...	41.60	0.90	1.380	N_6
		0.00	42.03	.00	1.378	N_6
	0.00	...	0.00	12.05	1.115	I_4
	6.88	16.69	7.78	9.00	1.141	I_4
	13.95	14.49	15.17	7.31	1.186	I_4
	21.62	14.18	24.35	5.58	1.253	I_4
50°	28.21	14.01	32.15	4.36	1.321	I_4
	34.79	11.62	38.82	3.57	1.368	I_4
	...	...	**44.41**	3.13	...	$I_4 + N_6$
	...	...	45.27	1.52	...	N_6
	...	0.00	46.09	0.00	...	N_6

N_6 represents $Mg(NO_3)_2 \cdot 6H_2O$

The solid phases at these three temperatures are determined beyond question by the extrapolation of the tie-lines from the composition of the saturated solution through the composition of the original complex used. At 5° there are found not only the hexahydrated magnesium nitrate and the decahydrated magnesium iodate, but also the tetrahydrated magnesium iodate in those solutions where the vapor tension has been greatly lowered by the highly soluble magnesium nitrate. At 25° only the two salts, each stable in water at this temperature, are found. At 50° the same condition prevails; were it not for the strange behavior of the magnesium iodate tetrahydrate already stated, one would be ready to predict that the anhydrous form should also appear, since the high concentration of magnesium nitrate obviously lowers the vapor tension greatly. The extrapolated tie-lines however point to the tetrahydrate as solid phase in every instance.

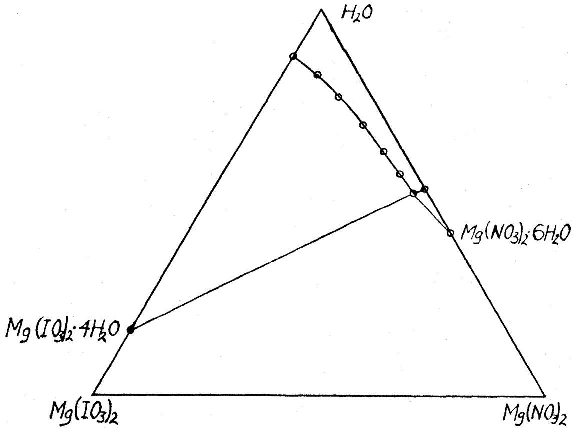

Fig. 4.—50° Isotherm: $Mg(IO_3)_2$–$Mg(NO_3)_2$–H_2O.

Summary

1. It is found that magnesium iodate and water give not only the decahydrate and tetrahydrate previously known, but also an anhydrous form stable in contact with water above 57.5°.

2. The solubility of magnesium iodate in water has been determined from −0.36°, the eutectic temperature, to +90°.

3. Ternary isotherms have been studied for magnesium iodate, magnesium nitrate and water at 5, 25 and 50°. No double compounds have been found.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS, AND THE UNIVERSITY OF OKLAHOMA, NORMAN, OKLAHOMA]

LITHIUM CHLOROPLATINATE AND THE SEPARATION OF POTASSIUM FROM SODIUM AND LITHIUM BY THE UNMODIFIED ORIGINAL FRESENIUS METHOD

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

RECEIVED DECEMBER 22, 1930 PUBLISHED MARCH 6, 1931

Introduction

The determination of potassium as potassium chloroplatinate is of sufficient historical interest to warrant a somewhat detailed reference to the literature of the subject as a theoretical background to the present paper. The original work of Fresenius on the separation and determination of potassium in presence of sodium and lithium by the chloroplatinic acid process consisted of two contributions.[2,3] Somewhat later there appeared an additional paper[4] by Fresenius consisting of a duplication of the former work. This confirmatory work was necessitated by the intervening revision of the atomic weight of platinum by Seubert[S] as will be explained later. Other important work dealing with Fresenius' process was contributed by Precht,[6] Dupré,[7] Morozewicz,[8] and Fresenius and Brinton.[9]

By the original Fresenius method,[2,3] of 1876–1877, potassium chloride was separated from sodium and lithium chlorides by converting the three chlorides to chloroplatinates, using an excess of chloroplatinic acid followed by the extraction of K_2PtCl_6 from the soluble sodium and lithium chloroplatinates using 80% ethyl alcohol. The value for the ratio $2KCl/K_2PtCl_6$ was found to be 0.3056. This value is the theoretical one based on the early atomic weight 197.18. In 1881 the Seubert[K] revision of the atomic weight of platinum established the value 194.46. Consequently, the German potash industry solicited Fresenius to reinvestigate his process, which was undertaken in 1882.[4] "As a result," Fresenius reported, "of all these determinations not the slightest doubt remains that for the calculation of the potassium chloride from the weight of potassium chloro-

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

[2] Fresenius, *Z. anal. Chem.*, 15, *224* (1876).

[3] Fresenius, *ibid.*, 16, 63 (1877).

[4] Fresenius, *ibid.*, 21, 234 (1882).

[5] Seubert, *Ann.*, 207, 1 (1881).

[6] Precht, *Z. anal. Chem.*, 18, 509 (1879).

[7] Dupré, Diss., Halle, 1893.

[8] Morozewicz, *Bulletin Inter. de L'Acadêmie des Science de Cracovie*, 796 (1906).

[9] Fresenius and Brinton, *Z. anal. Chem.*, 50.21 (1911).

platinate dried at 130°, no other value than 30.56 to 100 is permissible and if the Seubert ratio 0.3069 is employed high results necessarily follow." The inference derived from this statement was that the Seubert revision of the atomic weight of platinum should be confirmed. This was done by Halberstadt,[10] who substantially confirmed Seubert's value. The retention of the Fresenius value for the ratio $2KCl/K_2PtCl_6$ of 0.3056 therefore stamps the Fresenius method as empirical. Further studies of this method by Dupré[7] and Fresenius and Brinton[9] were attempts to clear up the difficulties involved. These failed to indicate methods eliminating the empiricism of the Fresenius method. The present value for the atomic weight of platinum, 195.23, was the result of the work of Archibald,[11] which gives for the theoretical factor 0.3067 as compared to the empirical factor 0.3056.

Variable Factors Influencing the Fresenius Method.—The basic facts accounting for the formation of impure precipitates of K_2PtCl_6 are summarized here. The chloroplatinic acid is often prepared under conditions giving the impurity $H(NO)PtCl_6$. This product results from the incomplete removal of the nitric acid used in the solution of platinum black with aqua regia. The complete removal of this nitric acid using hydrochloric acid results in the accumulation of the impurity $H_2Pt(OH)Cl_5$. Impurity in the precipitated K_2PtCl_6 results from the impure chloroplatinic acid as well as from the presence of water in the 80% alcohol, thus

$$K_2PtCl_6 + HOH = K_2PtOHCl_5 + HCl$$[12]

Absolute alcohol cannot be used to avoid the hydrolysis of K_2PtCl_6 for the reason that sodium chloride is thus formed from the Na_2PtCl_6 present:

$$Na_2PtCl_6 + \text{absolute alcohol} = 2NaCl + PtCl_4$$[13]

All these errors give rise to low results in the determination of the ratio $2KCl/K_2PtCl_6$. The effects of these errors are shown by the many methods for the analysis of K_2PtCl_6. For example, the platinum may be reduced to metal, separated by filtration from the soluble potassium chloride and weighed as such. The filtrate from the platinum determination may be evaporated to dryness and the potassium chloride determined. In this case hydrogen is used to precipitate the platinum. The chloride aside from that combined as potassium chloride can be determined by thermal decomposition with absorption of the hydrogen evolved and precipitation

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[10] Halberstadt, *Ber.*, 17, 2962 (1884); *Z. anal. Chem.*, **25**, 296 (1886).

[11] Archibald, *Z. anorg. Chem.*, **66**, 169 (1910); *Proc. Roy. Soc. Ed.*, **29**, 721 (1910).

[12] This reaction has led to the suggestion that K_2PtCl_6 should be separated in the presence of a small amount of hydrochloric acid.

[13] This fact was not recognized by Precht,[6] who proposed using absolute alcohol, but was corrected by Morozewicz.[8] The use of absolute ethyl alcohol is attractive for the reason that it diminishes the solubility of K_2PtCl_6 and is a better solvent for Na_2PtCl_6 and Li_2PtCl_6.

with silver. By the same method the total water can be determined. Water combined in the form $K_2PtOHCl_5$ is determined by ignition in an atmosphere of carbon monoxide followed by the determination of the carbon dioxide formed. Following these methods the exact determinations of the impurities in a precipitate of K_2PtCl_6 were studied by Dupré.[7] Since the dissertation by Dupré was not published in any other form, and since the material is almost inaccessible, a summary of this thesis is given.

Summary and Conclusions from the Work of Dupré

1. The determination of potassium in the form of chloride by the reduction of the platinum with hydrogen, followed by filtration and evaporation of the potassium chloride solution, gives accurate results after taking into account the solubility of K_2PtCl_6 in alcohol. This method of determining potassium chloride is independent of atomic weights, factors and variations in the conditions of the separation. The method is slow, involved and not adapted to routine application.

2. The separation and determination of potassium as K_2PtCl_6 from the direct weight of the precipitate gives good results if the factor for potassium chloride is 0.3056. Precision in the result thus obtained is the only justification for the use of this empirical factor.

3. Potassium chloroplatinate obtained using the Fresenius method does not have the exact composition K_2PtCl_6 but contains more platinum and less chlorine than indicated. The determination of its potassium chloride content is not correct if calculated from the determination of either the platinum or chlorine using either the Fresenius factor or the correct atomic weight for platinum.

4 Precipitates of K_2PtCl_6 obtained by the use of either sodium or lithium chloroplatinates to precipitate potassium chloride solutions, "evidently" likewise contain too much platinum and too little chlorine.

5. The methods for the analysis of K_2PtCl_6 depending upon the calculation of potassium chloride from the weight of platinum by hydrogen, sodium formate or metallic magnesium, all lead to incorrect results. The determination of chlorine using finely divided silver or following ignition at 500–550° using excess of sodium oxalate likewise gives erroneous results.

Lithium Chloroplatinate as Precipitant for Potassium Chloroplatinate.—The present work describes a process for the precipitation of potassium chloroplatinate in the presence of sodium in which the potassium chloride in the precipitate can be calculated from its weight or by determination of the platinum content. The purity of the K_2PtCl_6 thus precipitated is further proved by the fact that it is stable at 260°, whereas the salt precipitated using chloroplatinic acid decomposes at temperatures much above 160°. The preparation of lithium chloroplatinate is described. By this process there is obtained the theoretical factor for the ratios $2KCl/K_2PtCl_6$ and Pt/K_2PtCl_6.

At the time this work was begun the content of the dissertation by Dupré[7] was not familiar to the authors. As a result the process employing lithium chloroplatinate was thought to be original. A copy of the thesis was subsequently obtained and the errors in Dupré's work were studied. He stated that lithium chloroplatinate was unsatisfactory.

It should be pointed out that the present work does not indicate that the platinum process is the best for the separation of sodium and potassium. The separation of potassium from sodium and lithium using perchloric acid has been the subject of an extended series of researches by one of the present authors[14] and it has been shown that the use of perchloric acid for separations and determinations in the alkali group is superior to the platinum process in speed, accuracy and economy.

Experimental Part

Preparation and Purification of Materials

Lithium Carbonate.—An ordinary grade of lithium carbonate was suspended in a large volume of water in a flask and dissolved by conversion to the bicarbonate using a rapid stream of carbon dioxide during a period of several hours. The solution was filtered and the filtrate boiled to dissociate the lithium bicarbonate to the normal carbonate, which was precipitated, filtered and the mother liquor removed by centrifugal drainage. A portion of this product was dissolved and reprecipitated. The products thus obtained were used to prepare lithium chloroplatinate without further treatment. Both fractions were equally satisfactory.

Lithium Chloroplatinate.—Lithium carbonate was dissolved in either a slight excess or slight deficiency of reagent quality chloroplatinic acid, the solution filtered and the filtrate concentrated until upon cooling a slush of crystals and mother liquor was obtained. The crystals of hydrated lithium chloroplatinate ($Li_2PtCl_6 \cdot 6H_2O$) were filtered using a sintered glass filtering crucible and drained centrifugally in the same container. They were dissolved in water and recrystallized in the same way. In case the lithium carbonate had been dissolved in a small deficiency of chloroplatinic acid, a little more of the latter was added to the filtered solution before crystallization. The light yellow crystals of $Li_2PtCl_6 \cdot 6H_2O$ were found to be completely soluble in ethyl alcohol and were dried in a desiccator over anhydrone until ready for use. A yield of 65–70% of the total lithium chloroplatinate is easily obtained by this process. A second crop of 15% of the original quantity was then obtained.

Chloroplatinic Acid.—Crystals as purchased on the market.

Potassium Chloride.—This was from a stock of 100% KCl used in previous work, dried by fusion and proved to be pure by conversion to perchlorate by evaporation with a slight excess of pure perchloric acid. Occluded perchloric acid was removed by dissolving in hot water and evaporating to dryness. The crystals of potassium perchlorate now contained a small amount of occluded water which was removed by heating to constant weight at 350°. The final product gave no test for chloride. The purity of the potassium chloride was proved by the value obtained for the ratio $KCl/KClO_4$. The data are tabulated in Table I.

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[14] Willard and Smith, This Journal, 45, 2072 (1923); Smith, *ibid.*, 47,762 (1925); Smith and Ross, *ibid.*, 47, 774 (1925); 47, 1020 (1925).

TABLE I

THE CONVERSION OF POTASSIUM CHLORIDE TO POTASSIUM PERCHLORATE AND THE DETERMINATION OF THE RATIO $KCl/KClO_4$

	$KClO_4$ found			Factor $KCl/KClO_4$		
KCl, g.	15 min. 350° g.	Constant wt. 350°, g.	Error, $KClO_4$, mg	Found	Calcd	Error
0.15555	0.28915	0.28915	+0.1	0.53796	0.53816	—0.00016
.11580	.21530	.21530	+ . 1	.53786		— .0003
.11645	.21650	.21650	+ .1	.53788		— .00028
.15925	.29620	.29620	+ .3	.53764		— .0004
			Average	.53788		— .00028

Alcohol.—Reagent alcohol was refluxed over lime and distilled, giving a 99.6% product.

Sodium Chloride.—From a stock of material comparable to the pure potassium chloride described above.

Procedure Followed in Determining the Conversion Factor $2KCl/K_2PtCl_6$.—Weighed samples of pure potassium chloride were dissolved in water in 150-cc. beakers and a small excess of a solution of lithium chloroplatinate in water added to convert the potassium chloride to chloroplatinate. The precipitated K_2PtCl_6 was dissolved by heating and the greater portion of the water evaporated until upon rapidly cooling the hot solution a finely divided precipitate was obtained. The beaker and moist contents were treated with 25 cc. of absolute alcohol and the K_2PtCl_6 filtered using platinum sponge filtering crucibles. The precipitates were washed by decantation with fresh portions of absolute alcohol and transferred to the filtering crucible. The precipitates were then washed in the crucible by the addition of 10–15 separate small portions of absolute alcohol followed by drying first at 130° for extended periods of time and finally at 260° during two and one-half hours. The results of five consecutive determinations are listed in Table II.

TABLE II

RESULTS OF DETERMINATIONS

		K_2PtCl_6 Found					
Expt.	KCl, g	4 hrs , 130°, g	12 hrs , 130°, g	2 5 hrs , 260°, g	Factor $2KCl/K_2PtCl_6$	KCl found, g	Error, KCl, mg
1	0.10845	0.35315	0.35315	0.35310	0.30687	0.10838	—0.07
2	.12460	,40585	,40570	,40560	.30720	.12433	— .27
3	.11450	.37325	,37325	.37325	.30676	.11449	— .01
4	.07820	.25460	....	....	.30715	.07809	— .11
5	.17395	.56645	....	...	.30709	,17375	— .2
				Average	.3070		
				Calcd.	.30673		

The lithium chloroplatinate used for the conversion of KC1 to K_2PtCl_6 in Table II was made from lithium carbonate which had been twice precipitated from its bicarbonate solution by boiling. The $Li_2PtCl_6 \cdot 6H_2O$ was recrystallized once and dried in a desiccator over phosphorus pentoxide.

Two and one-half grams was dissolved in 25 cc. of water and sufficient of this solution added to give approximately a 20% excess.

The filtrate and washings from the five determinations in Table II varied from 40 to 47 cc. No correction was applied to the values obtained for the weight of K_2PtCl_6 left in the filtrate and washings. Such a correction if applied would result in an average correction to the potassium chloride found of 0.12 mg. Applying the correction would reduce the value found for the conversion factor $2KCl/K_2PtCl_6$ to practically the theoretical value.[15]

The precipitates of K_2PtCl_6 obtained in Table II were dissolved in the filtering crucibles using a minimum quantity of hot water and the filtrates caught in 125-cc. Erlenmeyer flasks for determination of their platinum content. The platinum sponge filtering crucibles were then dried and weighed. Their final weight was compared with the original weight, and a small correction applied for the insoluble impurities accumulated throughout the analyses. This correction averaged 0.25 mg. Failure to have applied this correction would have tended to make the results obtained agree more closely with the theoretical value.

To the K_2PtCl_6 from the experiments of Table II dissolved in water as above described, a little hydrochloric acid was added and the platinum reduced to metal by the use of hydrogen under slight pressure which was kept in contact with the solutions at a temperature of approximately 80° for a period of twelve hours or until the solutions were colorless. The platinum sponge thus obtained was filtered using the same filtering crucibles in which the K_2PtCl_6 had been filtered, washed with hot water, dried and ignited. The results of these analyses are included in Table III.

TABLE III

THE DETERMINATION OF PLATINUM IN K_2PtCl_6 AND DETERMINATION OF THE RATIO Pt/K_2PtCl_6

Expt.	K_2PtCl_6, g.	Pt found, g.	Pt calcd., g.	Pt error, mg.	Factor found, Pt/K_2PtCl_6
1	0.35310	0.14200	0.14179	+0.21	0.40215
2	.40560	.16290	.16288	+ .02	.4016
3	.37325	,15005	.14989	+ .16	.4020
4	,25460	.10195	.10224	− .29	.4013
5	.56645	.22680	.22747	− .67	.4004
				Average	,40162
				Calcd.	,40157

From examination of Table III it is found that practically the theoretical weight of platinum was obtained from the analysis of the K_2PtCl_6 shown in Table II. The slight error is found to be of the same direction and magni-

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[15] A second series of results for the ratio $2KCl/K_2PtCl_6$ determined with a new preparation of Li_2PtCl_6 in which the K_2PtCl_6 was dried at 160–170° gave the following values for the factor: 0.30625, 0.30671, 0.30660, 0.30707, 0.30683; mean, 0.30668.

tude as that found in the case of the determination of the factor $2KCl/K_2PtCl_6$. The low values found in the case of the last two experiments of Table III are the only ones obtained in both Tables I and II which **do** not show the trend predicted.

The Stability toward Heat of Potassium Chloroplatinate Precipitated by Lithium Chloroplatinate.—The observation has been made repeatedly and was familiar to Fresenius and all subsequent investigators that the precipitate of K_2PtCl_6 obtained using chloroplatinic acid is not stable much above 130". This temperature was not thought to be sufficiently high to eliminate entirely occlusion of water and the temperature of 160" is sometimes recommended as it was by Dupré.[7] No statement was found which would indicate that precipitates of K_2PtCl_6 obtained following the Fresenius method can be heated at a temperature above 160° without decomposition. A temperature higher than this is never advised.

Potassium chloroplatinate when pure is known to be stable at 400°, as demonstrated by Noyes and Weber.[16] The K_2PtCl_6 used in their work had been prepared from chloroplatinic acid made from platinum black by electrolytic oxidation in the presence of hydrochloric acid as described by Weber.[16] It was thought appropriate, therefore, to determine the various ratios $2KCl/K_2PtCl_6$, Pt/K_2PtCl_6 and $4Cl/K_2PtCl_6$ using chloroplatinic acid from various sources, including acid prepared by the Noyes and Weber process. The data are reported in Table IV.

TABLE IV

VARIOUS CONVERSION FACTORS DETERMINED FOR K_2PtCl_6 USING H_2PtCl_6 FROM VARIOUS SOURCES

Source of chloroplatinic acid	Factor determined	Values obtained					Average	Calcd.	Error, %
Commercial	Pt/K_2PtCl_6	0.40117	0.40067	0.39928	0 40098	0.40083	0.40060	0.40157	−0.25
Commercial	$2KCl/K_2PtCl_6$	.30495	.30540	.30525	.30554	.30613	.30546	.30673	−0.38
B.S. elec. oxid.	$2KCl/K_2PtCl_6$	.30346	.30465	.30440	.30347	.30407	.30401	.30673	−0.89
Recovered Pt + HNO_3 + HCl	$2KCl/K_2PtCl_6$	.30366	.30321	.30283	.30386	.30269	.30342	.30673	−1.08
	$4Cl/K_2PtCl_6$	.28444	.28936	.29074	.28980	.28966	.28980	.29174	−0.63
	Pt/K_2PtCl_6	.39766	.39901	.39606	.39850	.39753	.39775	.40157	−0.95

The determinations of the various ratios of Table IV followed the procedure given for the determinations using lithium chloroplatinate as precipitant. The results in the first two horizontal rows were obtained using 99.6% ethyl alcohol. The remaining results were obtained using 80% alcohol with a solubility correction applied on the basis of one part of K_2PtCl_6 dissolved in 26,400 parts of alcohol, the corrections calculated averaging 1.5 mg. The last sample of chloroplatinic acid in Table IV

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[16] Noyes *and Weber, Bull. Bureau Standards, 4,345 (1908)*; Weber, THIS JOURNAL, 30. 29 (1908).

was prepared from scrap platinum dissolved in aqua regia and later precipitated as platinum black and again dissolved in aqua regia followed by the removal of the nitric acid by evaporation with hydrochloric acid. It had been made and used in connection with previous work by others published from these laboratories.

It will be noted by examining Table IV that the values obtained using chloroplatinic acid purchased in the usual manner from a reagent supply company gave values for the determination of the Fresenius factor $2KCl/K_2PtCl_6$ which duplicated the value 0.3056 as given by Fresenius. The chloroplatinic acid made from scrap platinum showed the poorest quality and the three factors obtained leave no doubt that the K_2PtCl_6 precipitated using this acid was impure. The errors found were all in the predicted direction, namely, too little platinum and chlorine and a molecular weight of K_2PtCl_6 less than the theoretical.

A point of particular interest lies in the fact that the Fresenius method calls for the use of 80–85% alcohol for reasons cited above, whereas in the absence of sodium, absolute alcohol may be used, thus avoiding a correction due to the solubility of K_2PtCl_6. The correct Fresenius factor was obtained using 99.6% alcohol in the case of the first sample of $H_2PtCl_6\cdot 6H_2O$ of Table IV.

The Separation of K_2PtCl_6 from Na_2PtCl_6 Using Li_2PtCl_6 as Precipitant

In the practical separation of potassium and sodium using lithium chloroplatinate as precipitant two modifications of the procedure previously employed had to be applied. One consisted in using 80% ethyl alcohol in place of 99.6% strength. The reaction $Na_2PtCl_6 = NaCl + PtCl_4$ is known to occur[7] in the latter case. The sodium chloride formed is insoluble. The second modification consisted in restricting the filtrate from the K_2PtCl_6 in order to avoid the necessary correction for its solubility in 80% alcohol. This correction is undesirable since a variable excess of chloroplatinate ion makes the magnitude of this correction uncertain.

The use of the filtrate from the K_2PtCl_6 to transfer the precipitate to the filtering crucible made it possible to limit the filtrate and washings to a volume of 15 cc. That a complete transfer of the precipitate was obtained was shown by washing the beaker with distilled water which, after concentration to a small volume, was colorless. Using lithium chloroplatinate prepared as previously described, 80% alcohol as solvent and weighed quantities of potassium and sodium chloride, a series of separations was carried out using the theoretical factor $2KCl/K_2PtCl_6 = 0.3067$. The theoretical factor was obtained from the data. The K_2PtCl_6 precipitates were dried for an hour at 185° and finally for an hour at 200°. No decomposition resulted, as was proved by their complete solubility in hot water. Results are found in Table V.

TABLE V

THE SEPARATION OF POTASSIUM FROM SODIUM USING Li_2PtCl_6 AS PRECIPITANT AND 80% ALCOHOL AS SOLVENT

KCl, g	NaCl, g	K_2PtCl_6, g	KCl found using factor 0.3067, g	Error. KCl, g	Calrd. factor $2KCl/K_2PtCl_6$	Deviation from calcd., %
0.10565	0.190	0.34315	0.10525	−0.0004	0.30788	+0.37
.18160	.160	.59285	.18185	+ .00025	.30632	− .13
.21375	.130	.69815	.21410	+ .00035	.30617	− .18
.20110	.100	.65530	.20095	− .00015	.30688	+ .05
.11965	.090	.39060	.11980	+ .00015	.30632	− .13
			Mean[a]	− .00015	.3064	− .11

[a] Excluding the value for the first entry.

Reference to Table V shows that the theoretical factor for the ratio $2KCl/K_2PtCl_6$, namely, 0.3067, is obtained with an error of −0.1%. This theoretical factor was obtained using the detailed directions of the original Fresenius method with the one alteration, the substitution of lithium chloroplatinate for chloroplatinic acid. To include the value for the first determination of Table V would bring the mean value for the conversion factor closer to the theoretical.

Discussion of Results

In accord with the results obtained by all previous investigators the original Fresenius method using chloroplatinic acid, is found to be empirical. Using chloroplatinic acid purchased from a standard supply house, the Fresenius factor 0.3056 was obtained as compared to the theoretical 0.3067 Chloroplatinic acid from other sources or prepared from platinum residues may be less satisfactory.

The substitution of lithium chloroplatinate for chloroplatinic acid makes possible the use of the theoretical factor. The use of the lithium salt obviously does not permit determination of lithium in the presence of sodium and potassium It introduces lithium chloride into the filtrate from the potassium determination, which complicates the separation and direct determination of sodium. Several methods, however, are available for the separation of sodium from lithium.[14] The direct determination of sodium in the filtrate from the K_2PtCl_6 precipitation is seldom made, which minimizes this objection.

Lithium chloroplatinate to be used in the separation of potassium from sodium should be prepared from lithium carbonate purified by two precipitations from lithium bicarbonate and subsequent conversion to the normal carbonate, which is insoluble in water. An excess of lithium carbonate should be used in its conversion to lithium chloroplatinate using reagent quality of chloroplatinic acid.

The lithium chloroplatinate is twice recrystallized. One recrystallization improves the results but does not correct completely the errors resulting in low values for the'ratio $2KCl/K_2PtCl_6$.

It is of interest to compare the advantages afforded by the use of the chloroplatinate method for alkali metal separations with the disadvantages.

Advantages.—1. The insolubility of K_2PtCl_6 in 80% alcohol. One part of K_2PtCl_6 is dissolved by 26,400 parts of the alcohol

2. The low conversion factors $2KCl/K_2PtCl_6 = 0.3056$ (The Fresenius factor) or 0.3067 (Theoretical) and $K_2O/K_2PtCl_6 = 0.1906$.

3. The chloroplatinate process is a semi-extraction operation since the mixture of alkali chloroplatinates is taken up with alcohol from a concentrated solution in water. Occlusion of sodium and lithium chloroplatinates in the K_2PtCl_6 is therefore practically eliminated.

Disadvantages.—1. The cost of recovery of platinum. Aside from the cost of platinum and the interest on the value invested, the recovery is costly in time and attention.

2. The factor $H_2PtCl_6/2KCl$ is high, greater than 3.5. This value is greatly increased for the reason given in **3.**

3. The necessity for the conversion of NaCl to Na_2PtCl_6. The failure to complete this conversion results in the precipitated K_2PtCl_6 being contaminated by NaCl.

4. The direct determination of sodium in the filtrate from the potassium must follow the separation of platinum from the solution.

5. The method is empirical if H_2PtCl_6 is used.

6. Using H_2PtCl_6, the K_2PtCl_6 must be dried at 130°. Occluded moisture is not expelled completely at this temperature.

The low conversion factor in the original Fresenius method is due to the errors resulting from several sources. Reduction of platinum in H_2PtCl_6 is known to occur in warm alcohol solution. It was shown by Dupré[7] that precipitation of K_2PtCl_6 using a cold alcoholic solution of H_2PtCl_6 gave high results, indicating a low conversion factor $2KCl/K_2PtCl_6$. Presumably the addition of alcohol to the slightly acid solution that results from the precipitation of aqueous potassium chloride by aqueous H_2PtCl_6 also results in the reduction of platinum with the same effect. It is at least noteworthy that the use of lithium chloroplatinate for chloroplatinic acid avoids the formation of hydrochloric acid through precipitation of K_2PtCl_6. The hydrolysis of chloroplatinic acid to form such a product as $H_2PtOHCl_5$ would result in a high value for the ratio $2KCl/K_2PtCl_6$. Nitrosochloroplatinic acid, $H(NO)PtCl_6$, if present in the H_2PtCl_6, would have the opposite effect. The use of lithium chloroplatinate corrects these errors, as previously shown.

Summary

1. The preparation of lithium chloroplatinate suitable for a reagent in the precipitation of potassium has been described.

2. Potassium chloroplatinate of the theoretical composition is precipitated if lithium chloroplatinate is used in place of chloroplatinic acid, with 80% ethyl alcohol as solvent.

3. Precipitates of potassium chloroplatinate formed by the lithium salt are stable at 200–260°, whereas those obtained by the usual process are unstable at temperatures above 160°.

4. A critical discussion has been given of the errors involved in the old process and an explanation offered for the better results obtained by the new procedure.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF MCGILL UNIVERSITY]

THE DIELECTRIC CONSTANT OF WATER AS DETERMINED BY A RESONANCE METHOD

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RECEIVED DECEMBER 31, 1930 PUBLISHED MARCH 6, 1931

The object of this paper is not so much the determination of the dielectric constant of water, as an investigation of the adequacy for this purpose of the resonance method when employed in the manner previously described.[2] Certain criticisms have been put forward with regard to this method, the principal one being that when a measurable amount of conductivity can be assigned to the dielectric under investigation, the dielectric constant value obtained is irrelevant. It will be shown in this paper that criticism of the value found for the dielectric constant of water was justified, but that the error involved was due to a cause other than the conductivity of the water and that the method can be used for the measurement of the dielectric constant of water provided its conductivity is below a certain specified value.

It was suspected that any influence of conductivity was to be found in the absorption of the electric oscillations, with consequent distortion of the point of resonance. The set-up previously described was therefore altered to include a radiotron tube of greater power and measurements were made with dielectrics whose conductivity could be varied to a known extent by the addition of a small amount of electrolyte. Apart from this a method was devised for calibrating the tuning condenser. The effect of using the harmonic instead of the fundamental for the point of resonance

[1] Acknowledgment is hereby made of a studentship granted to one of us by the Research Council of Canada.

[2] Cuthbertson and Maass, THIS JOURNAL, 52, 483 (1930).

was also examined. For the determination of the absolute value of the dielectric constant of water a series of intermediate liquids was employed such that for each variation in the number of plates in the dielectric cell three liquids could be used so as to give a double check on the values obtained in each stage.

Changes in Set-Up.—The apparatus and dielectric cell used have been described in detail.[2] As source of oscillations the only important change made was to make it possible to replace the UX171A radiotron tube at will by a UX210 radiotron power tube giving at least ten times the wattage rating and using 368 volts on the plate. In order to keep a constant filament current three 6-volt accumulators in parallel were employed. It was necessary to change both honeycomb and choke coils so as to carry the increased plate current, which could be varied from 15 to 75 milliamperes. Both the variable and fixed oscillators were shielded and care was taken to have a constant temperature environment during the course of related observations, which were all carried out at 25°.

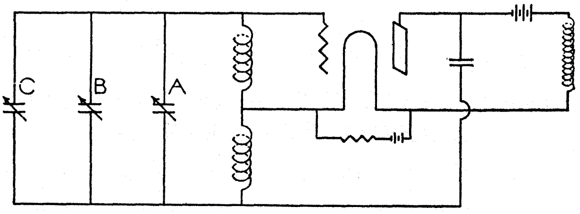

Fig. 1.—Set-up for calibrating tuning condenser **A**.

Calibration of Condenser.—The following procedure is worth describing as a useful method for calibrating the tuning condenser, not as far as its total capacity is concerned (which is of no interest), but in terms of its relative settings along the scale. In Fig. 1, which is similar to the variable oscillator previously described, **A** is the tuning condenser with a mirror mounted at the center of the dial so that scale readings could be read by reflected light on a circular scale four feet in diameter. The vernier control was manipulated by a pulley with 2 cord belt leading to a wheel placed at such a distance that its manipulation could be carried out without bringing in body capacity effects.

C connected in parallel is a variable condenser with the capacity arranged to correspond to a change of about 50 scale divisions on the tuning condenser between two fixed points of C. B also in parallel is a variable condenser with about the same capacity as the tuning condenser. The two fixed points of condenser C correspond to a capacity unaltered by any change in the set-up. By altering B, various parts of the scale readings of the tuning condenser could be calibrated in terms of this arbitrary but reproducible variation in the capacity of condenser *C*. **As** an analogy to this procedure one need only think of the calibration of a capillary tube by measuring the length of a mercury column as it is moved along the tube.

The tuning condenser was found to vary by several per cent. for different parts of the scale, but this variation was found to be perfectly reproducible and could therefore be corrected for in the subsequent measurements which were made. Table I gives a set of readings that were made to show the nature of the variations found.

TABLE I

CALIBRATION OF TUNING CONDENSER

Initial position on scale	7.0	21.0	36.4	54.5	71.6	93.6	114.2	134.8	159.0	175.9
Scale interval	50.7	51.1	51.4	51.8	52.0	52.1	52.2	52.3	52.2	52.1

With reference to the measurements previously reported which had been made with this same tuning condenser[2] it may be stated that, where a pair of liquids were compared over exactly the same range, the calibration is of course superfluous. Since, however, with two liquids that differ widely in dielectric constant the same range of scale may not be covered, an error may have crept in. Another advantage of the calibration was made evident by the fact that with the corrected scale readings all irregularity in the tuning condenser disappeared and since the dielectric cell condenser was also found to vary in a linear manner, the points obtained fall far better on a straight line.

Dead Space Correction.—As was to be expected, the interchange of the UX171A radiotron tube with the power tube showed no difference in the relative slopes of the curves obtained when two non-conducting media were compared in the dielectric cell. Also, the ratio of the slopes obtained for nitrobenzene and conductivity water when measured first with a 171A tube and then with the power tube agreed within the error of the measurements.

Another source of error which was suspected in the previous measurements was that in using the fundamental for the resonance point a large scale interval exists between the "no-sound" point when approached from the right or the left. If this scale interval has no variation for different settings of the dielectric cell no error may result. When the harmonic is used, which is more readily discerned with the aid of a power tube, this scale interval is reduced to an insignificant amount. In the following table data are given showing the scale readings for the fundamental when approached from the right and when approached from the left, and in the third column the scale readings given when the harmonic was used.

Table II

Scale Readings Giving Slopes

Dielectric cell	Right fundamental	Left fundamental	Harmonic
20	58.9	65 5	27.5
30	89.9	95 3	57.7
40	120.3	125 6	88.2
50	151 4	155 4	118 8
60	182 5	185 8	149 2
70	212.0	214 7	178 5
Slope =	153.1	149 1	151.0

Average, 151.1

It is evident that the "no-sound" scale interval ("dead space") varies with the setting of the dielectric cell. This is indicated by the values for the slopes of the lines given at the foot of each column. It will be observed that the mean of the slopes given by the left and right fundamental "no-sound" points is the same as that of the harmonic in which there is not what may conveniently be termed "dead space." The conclusion is that where the fundamental is used and a large "dead space" exists, the average of the right and left scale readings must be taken to plot the slope. Better still the harmonic should be used when with the aid of the power tube this can be discerned. With liquids having a small dielectric constant the fundamental gives right and left "no-sound" points which are close together and which do not vary appreciably in "dead space" intervals. This had been observed, and the mistake made in the previous results was in assuming that the same would hold for liquids of high dielectric constant.

Conductivity of Medium.—If the conductivity of the medium when at all appreciable distorts the resonance point, then the resonance method is open to unanswerable criticism. To investigate this point a series of experiments was carried out both with a medium having a small dielectric constant (ether) and one having a high one (water) in each of which variation of the conductivity of the medium could be obtained by the addition of electrolytes. In the case of water actual conductivities were measured and corresponding "slopes" determined. In the case of ether carefully purified hydrogen chloride gas was added in known amounts and the slopes of the resulting solution measured. Furthermore, in the case of water the effect of altering the power of the oscillating set and its influence on the slopes of various solutions was examined.

In Table III are given the normalities of hydrogen chloride–ether solutions and the corresponding apparent dielectric constants calculated on the basis of 4.255 for pure ether. The results are plotted in Fig. 2.

TABLE III

RELATION BETWEEN CONDUCTIVITY AND DIELECTRIC CONSTANT FOR ETHER

Normality	Slope	E	Normality	Slope	E
0	56.7	4.255	0.090	59.5	4.47
0.0061	56.7	4.255	.121	60.8	4.57
.013	56.6	4.244	.223	65.6	4.93
.024	56.7	4.255	.314	71.1	5.34
.038	57.3	4.30	.388	101.9	7.65
.052	58.0	4.35			

Conductivities of the ether solution have not been measured, but are roughly proportional to the hydrogen chloride concentration. It will be seen that the true dielectric constant of ether is approached in an asymtotic way with decreased conductivity. It may be safely assumed that provided the conductivity is below a certain value further decrease in conductivity does not measurably alter the value obtained by the resonance method.

The above was still more thoroughly investigated in the case of water. Table IV gives the values of the apparent dielectric constants of the water solutions as calculated from the slopes and based on a value of **79.20** for pure water. Column **A** of the table gives the results obtained with the UX171A tube; column **B** the values obtained with the power tube using a current of 20 m. a ; column C the values obtained with the power tube using 60 m. *a.*

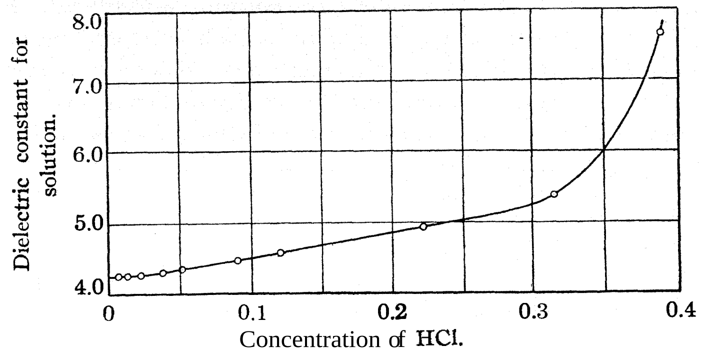

Fig. 2.

TABLE IV

EFFECT OF CONDUCTIVITY ON DIELECTRIC CONSTANT OF WATER AT 25°

	Dielectric constant		
Conductivity mhos 10^6	*A* 171A tube	B UX210 tube 20 milliamp.	C UX210 tube 60 milliamp.
1.31	79.1		
3.3	79.0		
4.0	79.2	79.2	79.2
5.0	80.7		
5.6		80.5	80.5
6.6	82.9	81.8	81.4
7.5	84.5		
8.1		83.5	82.4
9.9	95.5		
12.0	101.8		
13.0		88.2	86.6
24.0		99.8	96.7
34.0		144.0	136.8
44.0			182.0

The results can best *be* correlated by means of Fig. **3,** in which curves are lettered to correspond with the letter of the column in Table IV. It will be noted that in all cases the dielectric constant of conductivity water is approached asymptotically and that below a conductivity of 4×10^{-6} no difference in values is obtained; with increase in conductivity the values obtained alter with conductivity increasing rapidly in magnitude beyond a certain point. The effect of increased power in the oscillator flattens out the curve, decreasing the influence of the conductivity of the medium. It would appear from the nature of the above curves that as long as the conductivity is below a certain value, depending on the power used, a true value of the dielectric constant is obtained. Furthermore, this is not a question of extrapolation such as would be necessary were the curve a straight line. The fact that the curve is apparently asymptotic to the value obtained for the medium when a non-conductor, greatly enhances the validity of making use of the resonance method.

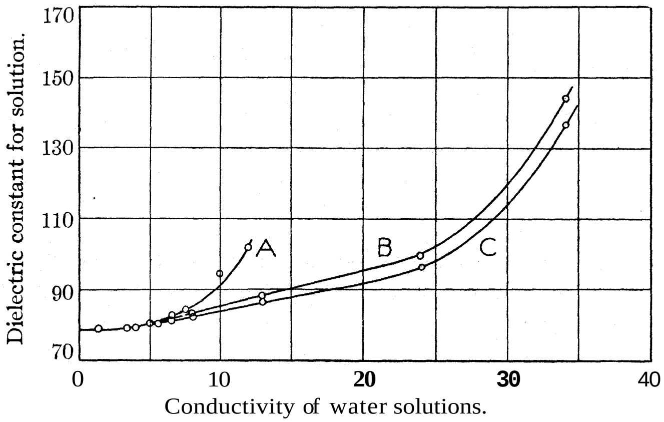

Fig. 3.

The emphasis brought about by recapitulation is perhaps warranted. It is true that the dielectric constant of water calculated from the slopes gives too high a value when the water conducts but the same limiting value is reached (independent of the power) when the conductivity is below 4×10^{-6}. It might be argued that since the purest water obtainable is still a conductor, this affects the value for the dielectric constant. In answer to this the experiments with ether show that with decreased conductivity the value obtained corresponds with that for pure ether, which is presumably a non-conductor. This value for ether, also, is in agreement with that found by other investigators.

Redetermination of the Dielectric Constant of Water.—The conclusion drawn from the above experiments is that the resonance method as described previously is not open to unanswerable objections. On the other hand, errors in the tuning condenser and dead space corrections would make it appear that the previous results referred to[2] need revision. Taking the necessary precaution in this connection the dielectric constant of water was redetermined by making use of benzene, ether, ethylene dichloride and nitrobenzene. The dielectric cell has been described in detail before.[2] This time for each set of stator and rotor' plates three media were used when possible as a counter check, and two series of investigations were made in each of which the dielectric cell was completely rebuilt.

TABLE V

DIELECTRIC CONSTANTS AT 25° OBTAINED IN VARIOUS SERIES FOR DIFFERENT CONDENSERS. EACH SET OF VALUES FOR A REBUILT CONDENSER

	17-Plate condensers	
Air	1.00	1.00
Benzene	2.273	2.270
Ether	4.250	4.258
Benzene average		2.271
	7-Plate condensers	
Benzene	2.271	2.271
Ether	4.255	4.250
Ethylene dichloride	10.38	10.34
Average of all ether values		4.255
	3-Plate condensers	
Ether	4.255	4.255
Ethylene dichloride	10.43	10.40
Nitrobenzene	35.30	35.20
Average of all ethylene dichloride values		10.38
	3-Plate condensers (with twice distance between plates)	
Ethylene dichloride	10.38	10.38
Nitrobenzene	35.1	35.2
Average of all nitrobenzene values		35 20
	3-Plate condensers (smallest capacity)	
Nitrobenzene	35.20	35.2
Water	79.40	78.9
Average for water		79.2

In the table the first substance in each set is taken as standard, the value having been derived from the previous set. Values could be repeated with the accuracy indicated for each condenser set-up. With condensers having a large capacity greater uniformity could be obtained. The three-plate condenser of smallest capacity introduced the greatest error and two extremes are given for the water–nitrobenzene pair. In Table VI the values found for the various substances are tabulated. Each had been carefully purified.

TABLE VI

DIELECTRIC CONSTANTS, T 25°

Liquid.............	Benzene	Ether	Ethylene dichloride	Nitrobenzene	Water
Dielectric constant...	2.271	4.255	10.38	35.20	79.2

Discussion of Results

If the value for water is calculated in different ways by using various pairs of liquids, the greatest divergence is about one per cent. Without again recapitulating the reasons that have been put forward in the first part of the paper, the authors are of the opinion that the resonance method as described can be used to give consistent results for the dielectric constant of a liquid such as water. The setting of the dielectric cell used involved a probable error of one-tenth to one-third of one per cent.; consequently in a series of stages (four in the case of water) the cumulative error may amount to 1%. Either a large number of observations will have to be taken or the dielectric cell improved. The authors are planning to investigate a cell of new design and redetermine the dielectric constant of water and also its temperature coefficient. In view of the results obtained the recalculated value for the dielectric constant of pure hydrogen peroxide at 0° is 93.5. By extrapolation of the dielectric constants of solutions of hydrogen peroxide in ether this value has been confirmed to within 0.5%.

Summary

The resonance method for the measurement of dielectric constants as described by Cuthbertson and Maass has been reinvestigated. A method for calibrating condensers, which vary in a linear manner according to their setting, is described. The effect of the power of the oscillating circuit has been examined and the precautions necessary in dealing with media of high dielectric constants specified, With a high power tube the harmonic is advocated as being better for the determination of the resonance point than the fundamental. The effect of the conductivity of the medium on the resonance point was shown to be negligible provided the conductivity was below 4×10^{-6} (in the case of water). Taking into account the necessary precautions the dielectric constant of water was found to be 79.2 at 25° by a step by step method based on 1.00 for air.

MONTREAL, CANADA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 257]

THE PRESSURE-VOLUME-TEMPERATURE VALUES FOR AMMONIA TO ONE THOUSAND ATMOSPHERES FROM 30 TO 200°

BY FREDERICK G. KEYES

RECEIVED JANUARY 3, 1931 PUBLISHED MARCH 6, 1931

The results herewith reported have been obtained from measurements carried out with the assistance of Mr. Robert B. Brownlee in 1913. It has been my intention to repeat the work using the improved apparatus which has resulted from a continuation of the program of measuring physical properties but a reexamination of the old results indicates that they are quite consistent enough to be of practical use. Moreover, it will be some time before new measurements can be made for liquid ammonia. The results are believed to be accurate with a maximum error of one-fourth per cent. The relative precision is much greater.

Apparatus Used.—The method and apparatus have already been described.[1] The pressures were obtained by using a piston gage of the type developed in this Laboratory.[2] The constant of the gage determined in 1911 before the present measurements were made was 4.1351[3] international mm of mercury per gram of weight on the piston. Bridgeman[4] has recently redetermined the constant of the same piston and found 4.1346 mm. using the value 26144.7 mm. for the vapor pressure of carbon dioxide at 0°.

Temperatures were determined by the use of the platinum resistance thermometer. The quality of the platinum available at the time of the measurements was inferior to that now in use in this Laboratory but the temperatures can only differ appreciably from the present scale[5] above 100°. In any case the temperature at 200° probably does not differ from the present scale by more than 0.05.

The volumes of the fluid under pressure are difficult to measure with the same precision as the pressures or the temperatures. Ordinary mild steel was used for the container and data for the elastic constants as a function of temperature were at the time not known. The temperature expansion

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[1] F. G. Keyes, J. *Am. Soc. Refrig. Eng.*, 1, 9 (1914); F. G. Keyes and R. B. Brownlee, THIS JOURNAL, 40, 25 (1918).

[2] F. G. Keyes and Jane M. Dewey, J. Optical Soc. *Am.*, 14, 491 (1927).

[3] F. G. Keyes and R. B. Brownlee, THIS JOURNAL, 40, 25 (1918).

[4] O. C. Bridgeman, *ibid.*, 49, 1174 (1927).

[5] The scale in use at this Laboratory at present is that based on the use of 0.1-mm. platinum wire with a mean temperature coefficient between 0 and 100° of 0.0039 or greater. The Callendar formula is employed using a δ value determined from the resistances at the ice, and boiling points of water and sulfur The normal boiling point of the latter is assumed to be 444.6°.

TABLE I

PRESSURE–VOLUME PRODUCTS FOR AMMONIA (UNITS, CC./G., ATM., DEGREES C.)

t	*V*, cc./g.										
	1.5	1.55	1.60	1.65	1.70	1.75	1.80	1.85	1.90	1.95	2.00
29.84	1548.0	1013.2	547.2	174.0							
34.86	1703.5	1161	681.5	308.1	31.0						
44.81	(1790.8)	1327	885.0	526.0	235.0						
49.83	(2052)	1576	1106	707.7	385.0	139.0					
54.88	(2070)	1604	1150	763.0	462.3	228.5	44.5				
64.88		(1800)	1371	986.0	676.0	424.5	222.0	64.5			
75.065		(2069)	1660	1263.0	936.0	671.0	453.5	285.8	148.5		
85.21		(2243)	(1882)	1519.5	1176	895.0	670.0	482.8	336.8	222.0	126.5
95.46			(2084)	1768	1451	1153	904.0	709.9	549.0	418.0	309.0
100.306			(2159)	1851	1537	1245	991.2	791.0	626.0	492.2	384.0
105.01			(2243)	1947	1651	1363	1107	893.5	724.0	583.0	472.0
115.01					1884	1610	1345	1122	938.0	788.0	661.2
129.862					(2082)	1859	1636	1423	1227	1060	918.2
139.51					(2236)	(2026)	1818	1609	1417	1250	1106
160.286							(2163)	(1977)	1792	1619	1466
180.709								(2312)	2143	1975	1819
200.701										2294	2140

t	*V*, cc./g.									
	2.05	2.10	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0
95.46	219.0	144.5								
100.306	297.0	224.5								
105.01	382.0	310.0								
115.01	557.7	474.4								
129.862	802.5	708.0	372.0	326.0						
139.51	985.0	884.0	493.0	428.3	453.2	508.8	564.2	620.0	676.0	731.8
160.286	1338	1227	760.5	646.8	650.0	697.5	748.5	804.0	860.0	913.2
180.709	1682	1566	1032	870.2	851.5	885.0	932.2	982.0	1032	1082
200.701	2002	1877	1302	1095	1055	1074	1112	1158	1206	1254

Conversion factors are as follows: (cu. ft./lb.)/(cc./g.), 0.016018; (lb./sq. ft.)/atm., 2116.2; Amagat units/(cc./g.), 0.0007715; (lb./sq. ft.)/atm. × (cu. ft./lb.)/(cc./g.), 33.9. The atmosphere is defined as the pressure per sq. cm. due to a column of mercury 76 cm. long at zero and *g*, 980.665, (the density of mercury being taken as 13.5951 g./cc.).

was likewise but inaccurately known (±3%). Means for determining the temperature dilation of the steel sample were not available. In computing the volumes given in the following tables the best available data have been employed. Nevertheless it is believed that the maximum error had best be assumed to be within one-fourth per cent.

Summary of Experimental Results

Rather than present the experimental results as obtained, it was decided to correlate the experimental data by means of graphs. A total of 191 volume and pressure measurements were available at 17 temperatures. The data were plotted to a large scale using pressure-volume products and volumes as coordinates. Table I gives the *pv* values at the actual temperatures observed for volumes from 1.50 cc./g. to 6 cc./g. In Table II, a table is given for even pressures from 100 international atmospheres to 1100 atmospheres and for each ten degrees of temperature to 200°. All numbers in brackets represent extrapolated values of the corresponding *pv* products.

Table II

Pressure–Volume Products for Ammonia (Units Cc./G., Atm., Degrees C.)

	$P_{\text{atm.}}$										
t	100	200	300	400	500	600	700	800	900	1000	1100
0	(155)	(316)	(458)	(612)	(757)	(900)	(1045)	(1189)	(1333)	(1482)	(1628)
10	158.5	318.5	466.0	619.3	766.8	911.0	1055	1200	1342	1489.5	1634
20	162.0	322.0	474.1	627.9	777.2	922.2	1066	1211	1353	1499	1643
30	165.8	327.5	482.5	637.0	788.8	935.2	1080	1224	1367	1511	1654
40	169.2	333.2	492.2	648.0	802.0	949.2	1096	1240	1382	1526	1669
50	173.0	340.7	503.8	660.5	816.8	965.0	1116	1259	1402	1545	1687
60	178.0	349.2	516.0	675.0	832.2	982.2	1135	1280	1423	1567	1709
70	183.7	359.0	529.2	690.0	849.5	1002	1156	1303	1448	1592	1735
80	190.0	370.7	543.2	706.5	868.2	1024	1179	1328	1473	1620	1764
90	199.0	384.2	558.7	725.2	888.5	1047	1203	1354	1501	1649	1793
100	208.2	399.5	575.8	745.5	910.0	1071	1228	1382	1530	1678	1824
110	223.5	416.0	594.8	767.2	934.0	1098	1255	1410	1560	1710	1857
120		436.0	617.2	790.5	960.0	1125	1283	1440	1591	1742	1891
130		462.0	643.5	817.8	988.2	1154	1313	1471	1623	1776	1926
140		498.5	674.0	848.0	1018	1184	1344	1502	1656	1810	1960
150		554.0	710.3	881.8	1050	1216	1376	1535	1690	1844	1996
160		638.0	751.7	919.2	1085	1249	1410	1569	1724	1879	2032
170		748.0	805.0	962.2	1124	1287	1446	1604	1761	1916	2069
180		887.0	869.0	1010	1168	1328	1481	1642	1798	1952	2108
190		1055	950.0	1068	1217	1370	1518	1680	1836	1992	2147
200		1255	1052	1128	1269	1416	1556	1720	1877	2032	2186
210									1921	2073	2225

Cambridge, Massachusetts

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ATOMIC WEIGHT OF IODINE. THE ANALYSIS OF IODINE PENTOXIDE

BY GREGORY PAUL BAXTER AND ALBERT QUIGG BUTLER

RECEIVED JANUARY 6, 1931 PUBLISHED MARCH 6, 1931

Introduction and Summary

In an earlier investigation by Baxter and Tilley[1] the ratio of silver to iodine pentoxide was found to be 0.646225, whereas on the basis of the more probable values of the atomic weights of silver and iodine,[2] 107.880 and 126.932, the ratio should be 0.646251. This puzzling discrepancy is in small part explained by the recent discovery in. this Laboratory by Mr. A. C. Titus[3] that the very porous iodine pentoxide, made by a process of double efflorescence from iodic acid, possesses the property of adsorbing air to the extent of 0.001%. The experimental ratio of silver to iodine pentoxide is thus raised to 0.646231, leaving a discrepancy between this value and that to be expected of 0.003%.

In **the** hope of discovering the cause of the discrepancy, and at the same time of obtaining a direct determination of the ratio of the atomic weights of iodine and oxygen, we have completed a series of analyses of iodine pentoxide by simple decomposition and weighing the iodine. This has already been done by Guichard,[4] but the results of his experiments were less concordant than could be desired and were subject to an uncertain correction for moisture retained by the iodine pentoxide.[5] The outcome of our work was unexpected, for we have found the ratio of iodine to iodine pentoxide to be almost 0.005% smaller than that corresponding to the modern value for the atomic weight of iodine, 126.932. Thus both this investigation and that on the ratio of silver to iodine pentoxide indicate that iodine pentoxide produced by dehydration of iodic acid contains less iodine (and more oxygen) than corresponds to the theoretical formula; for aside from the fact that the modern value for the atomic weight of iodine rests on several well-established ratios to silver and the other halogens, in order to reconcile the experimental values of the ratios of silver and iodine to iodine pentoxide with the theoretical values would necessitate an ***increase*** in the atomic weight of iodine of 0.005 unit in the former case and a ***decrease*** of 0.03 unit in the latter.

The Preparation **of** Iodine Pentoxide.—No pains were spared in the

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[1] Baxter and Tilley, THIS JOURNAL, 31, 201 (1909).

[2] Baxter, *ibid.*, 32, 1591 (1910).

[3] This investigation will soon be published.

[4] Guichard, *Compt. rend.*, 159, 185 (1914).

[5] Baxter, Tars JOURNAL, 37,411 (1915).

purification of this substance, and advantage was taken of much experience in this Laboratory in the purification of iodine and iodic acid.

Three kilograms of commercial iodine were distilled in portions from solution in concentrated aqueous potassium iodide. In this way the greater portion of chlorine and bromine were removed. A portion of the product was converted to potassium iodate by boiling with alkaline permanganate, and the iodate was converted to iodide at an elevated temperature. The remainder of the iodine was again distilled in portions from a concentrated solution of this potassium iodide. Thus the purification effected in the first distillation was made more nearly complete since the iodide was purer. Centrifugal rinsing of the product with pure water removed the greater part of any potassium iodide solution which might have accompanied the iodine vapor as spray.

Since iodine which has been purified merely by distillation from aqueous solution leaves a residue of organic matter when sublimed, this impurity was next removed by combustion in oxygen. The iodine was placed in a 20-mm. quartz tube connected at one end with a supply of carefully purified oxygen. Beyond the iodine the quartz tube was constricted to half diameter at two points, in such a way as to provide two compartments several centimeters long. The constrictions were filled with coils of platinum wire. The iodine was then sublimed in a current of oxygen into the first compartment through the first constriction which was heated to redness. A second sublimation followed, from the first to the second compartment, while the second constriction was heated. The twice sublimed material was then melted in the second compartment and poured into a vessel of pure water. The first distillation yielded a small amount of brownish residue, but the second yielded none. The presumption seems justified that organic impurities, even cyanogen, were removed in this treatment.

The iodine was next converted into potassium iodate by oxidation with potassium permanganate which had been twice recrystallized. Since this oxidation proceeds through the iodide, a small amount of potassium hydroxide was added to start the reaction. At first this latter was made by igniting a portion of the purified permanganate; later a portion of the alkaline solution resulting in the main reaction was used. Iodine and permanganate were mixed and boiled with an alkaline solution, sufficient iodine being used to complete the reaction with the permanganate. The solution of the iodate after standing was decanted from the precipitate of manganese dioxide, clarified by centrifugal settling and filtration through a sintered glass filter, and evaporated until saturated with potassium iodate. After the crystals had been removed, the mother liquor was further evaporated and a second crop obtained. All the potassium iodate was then once recrystallized.

The potassium iodate was converted into barium iodate by precipitation with barium hydroxide which had been twice recrystallized. Boiling hot normal solutions of both were used in the precipitation, the hydroxide being very slightly in excess. After standing for some time the precipitate was washed by decantation until the washings were nearly or quite free from alkali. In order to increase the efficiency of each washing the precipitates were centrifugally settled. The precipitate was then dried in platinum over an electric heater, and was found to weigh 2630 g. or about 45% of the theoretical yield from the original 3 kilograms of iodiie.

The final step in the series was the conversion of the barium iodate into iodic acid by metathesis with distilled sulfuric acid. A hot concentrated solution of a slight excess of sulfuric acid was added to the barium iodate suspended in hot water and the mixture was digested for several days in Pyrex flasks. After the supernatant solutions had been decanted, they were evaporated in platinum dishes. The precipitates were washed by decantation and the washings after evaporation in pyrex flasks were added to the main solutions. Since a small amount of suspended barium sulfate still remained, the solutions were filtered through a platinum sponge crucible into platinum dishes and after evaporation on electric heaters, were allowed to crystallize. The ordinary method of fractional crystallization was then followed as indicated in Fig. 1, where the crystal fractions are carried to the left, the mother liquors to the right. Because of the slowness with which equilibrium is established, each crystallization required several days. In the early steps of the process each fraction was divided into two or more portions for convenience and safety. Just before each final crystallization the solution was filtered through platinum sponge, although no insoluble matter could be detected. As soon as the crystallization process was commenced the material came into contact only with platinum.

In spite of these efforts the iodic acid at first possessed the peculiar odor which has been noted elsewhere.[6] This gradually disappeared from the purer fractions and was almost if not quite absent from each final crystal fraction.

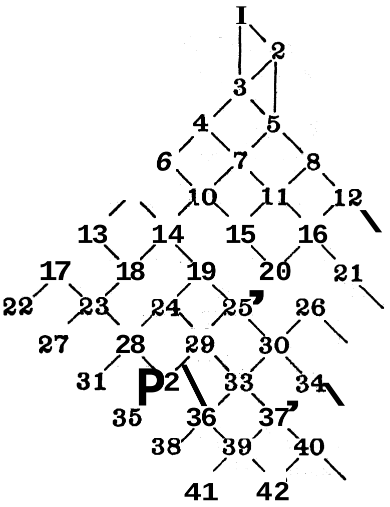

Fig 1.

Since sulfuric acid was present in the original solution, it was important to determine how rapidly this was eliminated in the crystallization. The usual test for sulfate is not sensitive enough for the purpose on account of the large amount of iodic acid necessarily present. A better method was found by heating the iodic acid in a current of air at 200–250° and passing the air through pure water, which was then tested for sulfate in the usual manner. In this way it was found possible to detect with certainty 0.2 mg. of sulfuric acid in 5 g. of iodic acid. Using this method the mother liquor 40 was found to contain 0.05–0.10 g. of sulfuric acid, while none could be detected in mother liquor 42.

Further tests for sulfate were combined with tests for non-volatile matter by decomposing 5-g. portions of the final crystal fractions in weighed platinum or quartz boats and determining the weights of the residues.

Fraction	Boat	Sulfate, mg.	Residue, mg.
41	Pt	0.03	−0.02
41	Pt	0	+ .07
31	Quartz	0	.00
22	Quartz	0	+ .03

Spectroscopic tests in a copper arc, using a Féry quartz spectrograph, failed to indicate the presence of barium except in the first mother liquor.

This evidence indicates that the purification by crystallization proceeded

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[6] Baxter and Tilley, THIS JOURNAL, 31,203 (1909).

rapidly and that the final crystal fractions must have been very nearly if not quite pure.

In all the foregoing operations the usual precautions in precise work were taken. Water was doubly distilled, first from alkaline permanganate, then from a trace of sulfuric acid, with tin condensers. Especial care was taken to insure protection from dust and fumes. Crystals were centrifugally drained either in an all porcelain centrifuge or in platinum Gooch crucibles.[1] Pyrex glass vessels were employed in the earlier operations, nothing but platinum during the crystallization of the iodic acid.

The Quantitative Decomposition of Iodine Pentoxide

The method of analysis consisted first in preparing iodine pentoxide for weighing by careful dehydration of iodic acid. The pentoxide was then decomposed by heating to about 400° in a weighed quartz reaction vessel which contained hot silver to prevent escape of iodine, and finally the weight of the iodine was determined. Water retained by the pentoxide was collected in a weighed absorbing tube and subtracted from the weight of the iodine pentoxide, as was also a correction of 0.001% for adsorbed air.

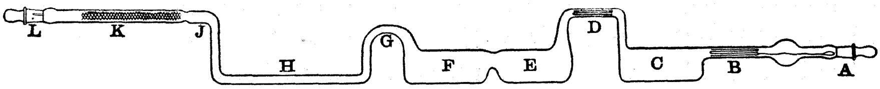

Fig. 2.

Since the possible accuracy of the process was limited by the weight of oxygen liberated, which constitutes less than one-quarter of the weight of the pentoxide, comparatively large quantities of pentoxide were used in each experiment, usually over 40 g. Necessarily the reaction tube was of considerable size and weight. After various preliminary experiments with a reaction tube made of pyrex glass, the final tube of fused quartz was constructed as indicated in Fig. 2. The air current entered through the ground joint A which was provided with a carefully ground stopper. At B was placed a coil of platinum wire which could be heated to redness from the outside. The tube D connecting the decomposition chamber C, 30 × 75 mm., which served to contain the iodine pentoxide during the initial weighing, and the iodine condensation chambers E and F, contained a coil of platinum wire which was heated to redness during an experiment. Condensation of iodine was made as complete as possible in H and the small amount of uncondensed iodine was collected in K upon metallic silver heated to about 600° by means of a removable resistance coil. During an analysis E, F and H were immersed in an ice-bath. A weighed U-tube containing resublimed phosphorus pentoxide was attached by a ground joint at L, which also was provided with a carefully ground stopper. Be-

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[1] Baxter, This Journal, 30, 286 (1908).

cause of limitation of space in the balance case the apparatus was bent back on itself at D, G and J, so that the inlet A and the outlet L were not far apart. The weight of the empty system was 143 g. In order to avoid any effect from changing atmospheric conditions between the initial and final weighings, a counterpoise was provided of very nearly the same construction. The weight and volume of the counterpoise were made very nearly the same as those of the tube by adjusting with pieces of platinum and silver wire, and of quartz, the weight of the counterpoise being slightly less than that of the tube. In the early experiments the counterpoise was of pyrex glass, but in the later ones a quartz counterpoise was used.

The method of weighing consisted in hanging the tube and counterpoise on opposite sides of a No. 9 Troemner balance of 500-g. capacity and sensitive to 0.02 mg. or less, and finding the difference in weight necessary to bring the system to the zero point of the empty balance taken directly afterward. The balance room was kept at constant temperature within two degrees so that variations of the ratio of the balance arms were avoided. The balance case was provided with two dishes containing a few milligrams of impure radium bromide to dispel electrostatic charges. During a portion of the time fused potassium hydroxide also was placed in the balance case, although no apparent benefit resulted from this.

In spite of these precautions many difficulties were experienced in weighing the tube, and more time was spent in overcoming these than in the actual analyses. Part of the difficulty undoubtedly resulted from surface effects on the quartz, for this material is notoriously troublesome in this respect. Uncertainty from this source eventually was eliminated by standardizing the preliminary treatment. That finally adopted consisted in wiping the surface with dilute hydrochloric acid, rinsing with water and wiping with a damp cloth just before placing on the balance. The counterpoise was wiped with a damp cloth at the same time. The weighing was carried out only after some hours, usually twelve to fourteen.

A far more troublesome irregularity was eventually traced to diffusion of water vapor from the outside into the tube, thus displacing the heavier air and causing a loss in weight. The amount of water vapor found in the tube, initially filled with dry air and allowed to stand, corresponded closely with the loss in weight of the tube which took place during this period when the difference in density of air and water vapor was taken into consideration. This loss in weight in one case amounted to 0.75 mg. in two days, even when the tube was closed except for narrow grooves in the stoppers necessary for equalization of pressure within and without. How much of this was due to simple diffusion and how much to small fluctuations in temperature is difficult to determine. The effect was considerably more noticeable in the late spring and summer months when most of the experiments were carried out than in the early spring when the preliminary ones were performed.

The difficulty was largely overcome by providing the tube with a stopper grooved for only half its length. The groove could be connected with the outside at will by turning the stopper until the groove registered with a small opening in the socket. In this way the tube could be kept essentially sealed until shortly before the weighing, when connection with the outside could be established by turning the stopper.

Even with the new stopper moisture was found very slowly to enter the tube, to the extent of 0.20 mg. in twenty hours, on an average as determined in four concordant experiments. With uniform treatment the reaction tube whether empty or containing iodine pentoxide or iodine would always be affected to the same extent, so that the weight of oxygen would not be affected if it were not for the fact that this water was collected in the phosphorus pentoxide tube. It is obvious that the weight of water collected in each experiment must be corrected for the water diffusing into the reaction tube.

The moisture content of the iodine pentoxide was found by passing the oxygen which resulted from the decomposition through a counterpoised U-tube containing resublimed phosphorus pentoxide. Iodine pentoxide which has been formed by dehydration of iodic acid at the temperature used in our experiments has been found to contain from 0.0025 to 0.0062% of moisture according to the method of preparation and time of heating.[6] In order to avoid the uncertainty involved in applying an average correction, the water was collected in each experiment. Since experience has shown the practical impossibility of securing absolute blanks in a water determination, the rate of gain of the phosphorus pentoxide tube was found in the air stream utilized in our experiments. The following table gives the results of these experiments.

Duration, hours	H_2O found, mg.		H_2O found per hour, mg
a	0.09		0.03
3	.13		.04
2.75	.11		.04
2	.08		.04
1.5	.09		.06
		Average	.04

The air stream itself was cleansed and dried by passing through a train containing the following agents: hot copper oxide, aqueous silver nitrate, aqueous potassium hydroxide, fused potassium hydroxide, concentrated sulfuric acid, phosphorus pentoxide, sintered glass filter. The system was constructed wholly of glass with dry, ground-glass connections.

To prepare iodine pentoxide from iodic acid, crystals of the latter were powdered in an agate mortar, usually together with a small proportion of the first phase formed in the dehydration, $HIO_3 \cdot I_2O_5$, since the water is then given off at a comparatively low temperature (80–110°) by efflorescence without melting, and moisture retained by the final product somewhat reduced.[8] The powder contained in platinum boats was placed in a quartz tube connected with the train for purifying and drying air and surrounded by an aluminum block furnace? The temperature of the furnace was first maintained at 100–110° as long as water appeared to be given off and then was raised to 200–210° to expel the remaining water of composition. Finally the material was heated to 240°, the highest temperature found by Baxter and Tilley to be safe, for about three hours. In many cases the product remained perfectly white, in others, especially if the temperature exceeded 240° or the period of heating was longer, a slight brownish tint appeared. Even when the iodic acid was free from odor, the iodine pentoxide made from it always possessed the peculiar odor which has been noted before.

In the meantime the quartz reaction tube had been prepared for weighing by passing a current of dry air through it and, after the treatment described on page 972 and standing for fourteen hours, was weighed. By means of a platinum thistle tube extending into the decomposition chamber C the iodine pentoxide was introduced without contaminating the inlet tube. The platinum coil B was then replaced, Dry air was then passed through the tube, while usually at the same time the chamber C was warmed to about 100°. If C was warmed the air entered at L so that iodine formed by incipient decomposition of the pentoxide could not come into contact with the silver. After cooling with the air current running, the tube was treated and weighed after fourteen hours as in the first weighing. After some time, about six hours, the quartz tube was rapidly attached both to the air line and to the phosphorus pentoxide tube, which also had been weighed. A second phosphorus pentoxide tube was used to protect the weighed tube from back diffusion of moisture. The chambers F and E were surrounded with ice and water and the tube K containing silver was surrounded by an electrically heated sleeve. The platinum coils B and D were heated to redness by Méker burners and the ground connections were cooled with wet cotton wicks. Then an air current was started and the chamber C was cautiously heated with a flame until decomposition of the iodine pentoxide proceeded slowly and uniformly. Usually about two hours were required for complete decomposition. Care was necessary to avoid rapid decomposition since the pentoxide itself was likely to be blown about if the reaction proceeded too rapidly. The hot platinum coils served the purpose of decomposing powdered material which might have been expelled from the decomposition chamber. Clog-

[8] Baxter and Tilley, Ref. 6, p. 210.

[9] Baxter and Coffin, *Proc.* Am. *Acad.*, 44, 184 (1909).

ging of the system with condensed iodine was likely to occur and was remedied by judicious use of a flame.

When decomposition was complete the ice-water bath was transferred to the tube H and the iodine sublimed from E, where the greater part originally condensed, to F where it was eventually fused. Except for the silver the whole system was then allowed to come to room temperature. Next the phosphorus pentoxide tube was removed, the stopper inserted at L, and the silver in K allowed to cool while at the same time the dry air was maintained inside at atmospheric pressure so that no moist air was forced in during the cooling. Finally, after it had been disconnected and the stopper inserted at A, the system was prepared for weighing as usual and weighed fourteen hours later. The experiment was completed by the weighing of the phosphorus pentoxide tube.

Although a considerable quantity of silver iodide was formed on the inner end of the silver column, the outer end remained untarnished. Furthermore, tests for free iodine in the air which passed through the system during an analysis were negative. It therefore is unlikely that any iodine was lost in the air current.

After an experiment the decomposition tube was attached to the air train in the reverse fashion by the joint L and cleaned by subliming the iodine into a pyrex flask. A very slight residue was allowed to accumulate in C (see page 970).

Weights were calibrated by the Richards substitution method, just before and just after the analytical work was carried out. In only two cases was the correction of an individual weight found to vary by 0.02 mg. in this interval, although differences of 0.01 mg. were found in the case of more than half the weights. In computing vacuum corrections the following densities were assumed:

Air (0° and 760 mm.)	0.001293
Weights	8.3
I_2O_5	4.799[10]
I_2	4.94[11]

Results

The following table presents the data for all analyses which were completed except one. Of these, three are subject to known errors, Nos. 1, 2 and 6. In one experiment, not included in the table, the procedure was so changed that it was impossible to determine the weight of the pentoxide or that of the water with certainty.

The weights of iodine pentoxide given in the third column have been corrected by subtracting 0.001% for adsorbed air. Since the iodine was chiefly in the form of a fused mass, with a relatively small proportion of

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[10] Baxter and Tilley, Ref. 6.

[11] "International Critical Tables," Vol. III, p. 21.

crystals of considerable size, the surface exposed was small and adsorption of air must have been at a minimum.

TABLE I

THE RATIO OF IODINE TO IODINE PENTOXIDE

Analysis	Crystal fraction	I_2O_5[a] in vacuum, g.	H_2O,[b] g	H_2O, %	Corr. wt. of I_2O_5 in vacuum, g.	I_2 in vacuum, g.	O_2 in vacuum. g.	Ratio $I_2:I_2O_5$	Ratio $I_2:O_5$
1	35	23.43598	0.00071	0 0030	23.43527	17.81810	5.61717	0.760311	3.17208
2	35	25.53039	.00215	.0084	25.52824	19.40949	6.11875	.760314	3.17213
3	35	42.46100	.00195	.0046	42.45905	32.28337	10.17568	,760341	3.17260
4	35	46.13494	.00186	.0040	46 13308	35.07699	11 05609	.760344	3.17264
5	22	46.22744	,00163	.0035	46.22581	35.14741	11.07840	.760342	3.17261
6	27	21.05743	.00181	.0086	21.05562	16.00913	5.04649	.760326	3.17233
7	27	22 07691	,00037	.0017	22.07654	16.78564	5.29090	,760338	3.17255
8	27	41.89153	.00179	.0043	41.88974	31.85032	10.03942	.760337	3.17253
9	41	42 71467	.00201	0047	42.71266	32.47602	10 23664	,760337	3.17253
			Average	.0043				,760332	3.17244
Average of Analyses 3, 4, 5, 7, 8, 9				.0038				,760340	3.17259
Extreme deviation of Analyses 3, 4, 5, 7, 8, 9								.000007	0 00011

[a] Less a correction of 0.001% for adsorbed air.

[b] Less a correction of 0.20 mg. for moisture diffused into the system before weighing and of 0.04 mg. per hour of duration of the experiment. See pages 968 and 973.

In Analysis 1 iodine vapor was lost from the tube owing to plugging with condensed iodine. In Analysis 2 a crack developed in the tube and in addition, owing to overheating, silver iodide sublimed from the silver section. In Analysis 6 a stopcock in the system was accidentally left open so that owing to insufficient pressure iodine was lost by back diffusion. In Analysis 7 the quantity of material was made about half the size of that usually employed in the hope that a constant error might be uncovered.

One other correction remains to be discussed. The air in the decomposition tube must have been nearly saturated with iodine vapor at the time of weighing and therefore the weight of the tube was less than it should be by the weight of air displaced by the iodine. Since the vapor pressure of iodine at 25° is 0.3 mm.[12] and the interior volume of the tube about 200 ml., the air displaced is 0.08 ml. under average conditions and the weight of iodine too small by 0.10 mg. The effect of applying this correction is to raise the observed ratios of iodine to oxygen and iodine pentoxide by 0.001 and 0.0003%, respectively, to 3.17262 and 0.760342.

The values for these ratios to be expected from the atomic weight of iodine now considered most probable, 126.932, are 3.17330 and 0.760381, differences of 0.021 and 0.005%. The difference between the observed values and those to be expected corresponds to a difference in the atomic weight of iodine of —0.027. In other words the atomic weight of iodine calculated from our experimental results is 126.905. It is difficult to believe that this value is correct. On the basis of the more probable value 126.932 the computed deficiency in iodine obtained experimentally amounts

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[12] Baxter, Hickey and Holmes, THIS JOURNAL, 29, 127 (1907).

to 0.0015 g. with a 40-g. sample of iodine pentoxide. This deficiency is far greater than the apparent experimental error.

The atomic weight of iodine calculated from the corrected experimental ratio of silver to iodine pentoxide, 0.646231, found by Baxter and Tilley, is 126.937, on the basis of the atomic weight 107.880 for silver, The coincidence is striking that the discrepancy in the composition of iodine pentoxide, though a little more than half as large, is in the same direction as that indicated by our experiments.

By combining the experimental ratios of silver and iodine to iodine pentoxide the ratio of iodine to silver is found to be 1.176579 and the atomic weight of iodine 126.929 on the basis of Ag = 107.880. This value for iodine differs very little from that found by direct comparison with silver, 126.932.

The percentage of iodine in iodine pentoxide is apparently too small, the percentage of oxygen too large. If the extra oxygen is wholly or in part in the form of a higher oxide, the oxidizing power of the iodine pentoxide should be too large. In a subsequent paper will be described a comparison of arsenic trichloride with iodine pentoxide in which it appears that this is the case. If the apparent excess of oxygen indicated by our work, 0.005%, is wholly in the form of the heptoxide, the proportion of the latter would be ten times as large.

We cannot avoid the conclusion, therefore, that iodine pentoxide of normal composition is difficult if not impossible to prepare and that conclusions based upon its actual composition are not sufficiently reliable for work of high precision.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

SALT AND MEDIUM EFFECTS ON THE TEMPERATURE COEFFICIENT OF VELOCITY OF DECOMPOSITION OF DIACETONE ALCOHOL[1]

BY GEORGE M. MURPHY

RECEIVED JANUARY 13, 1931 PUBLISHED MARCH 6, 1931

The hydroxide-ion catalysis of diacetone alcohol has recently been investigated by Åkerlöf,[2] who determined the influences of different hydroxides at various concentrations and both weak and strong hydroxides in salt solutions upon the reaction rate. Further, results were obtained by him which showed the effects on this reaction rate of addition of some alcohols and other organic solvents to the aqueous hydroxide solutions. Results contained in this investigation demonstrate the influences of the

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[1] The present study constitutes a part of a thesis presented to the Graduate School of Yale University as partial fulfilment of the requirements of the degree of Doctor of Philosophy, 1930.

[2] Åkerlöf, THIS JOURNAL, 48, 3046 (1926); 49, 2955 (1927); 50, 733 (1928).

addition of sodium chloride and methyl alcohol upon the temperature coefficient of reaction rate of the decomposition of diacetone alcohol catalyzed by suitable concentrations of sodium hydroxide. Measurements of the reaction rate at 20, 25, 30 and 35° in the presence of various strengths of sodium hydroxide between 0.01 and 0.1 molal have also been obtained.

Experimental Results

Since the measurements were made by means of a dilatometer and by a method similar to that described by Åkerlöf, little further need be added here. The temperature was controlled to within ±0.005° during a given measurement. Considerable care was exercised in the preparation of the solutions and the purification of the chemicals. The velocity constant was computed by the equation

$$K = \frac{1}{t} \log \frac{l_\infty}{l_\infty - l_t} = 0.434k \qquad (1)$$

where l_∞ is the length read on the dilatometer which corresponded to complete reaction, and l_t that which corresponded to the quantity changed in time, t. The over-all accuracy of this measurement is estimated to be approximately ±1%. Table I contains the results. The column headings are self-explanatory.

TABLE I

VELOCITY CONSTANTS AND TEMPERATURE COEFFICIENTS OF THE DECOMPOSITION OF DIACETONE ALCOHOL

$K \times 10^4 = 0.434k \times 10^4$

(1) **Sodium Hydroxide Solutions**

m (NaOH)	K_{20}	K_{25}	K_{30}	K_{35}	K_{30}/K_{20}	K_{35}/K_{25}
0.01	12.5	19.6	32.5	53.0	2.60	2.68
.02	26.0	40.0	67.0	106.0	2.58	2.65
.04	52.2	81.5	134.9	220.6	2.59	2.70
.05	65.5	104.1	167.5	279.4	2.56	2.68
.06	78.7	123.0	202.0	330.2	2.56	2.68
.07	91.5	144.8	234.9	385.6	2.57	2.66
.08	103.2	166.5	264.0	440.8	2.56	2.64
.10	133.5	210.0	350.2	565.6	2.62	2.69
					2.57	2.67

(2) **Sodium Hydroxide–Sodium Chloride Solutions**

NaOH (0.05) + NaCl (m)

m	K_{20}	K_{25}	K_{30}	K_{35}	K_{30}/K_{20}	K_{35}/K_{25}
0.00	65.5	104.1	167.5	279.4	2.56	2.68
.1	64.5	100.2	163.6	270.0	2.54	2.70
.2	63.6	98.5	162.6	265.4	2.56	2.69
.4	60.0	92.5	154.0	250.4	2.57	2.72
.5	58.0	89.0	149.0	242.6	2.57	2.73
.6	56.1	85.8	144.2	232.0	2.58	2.70
.8	53.2	81.0	137.5	219.5	2.60	2.71
1.0	50.8	77.8	132.0	208.5	2.60	2.72
					2.57	2.70

TABLE *I* (*Concluded*)

(3) Water–Methyl Alcohol Mixtures

$NaOH$ (0.1) + CH_3OH (C, %)

C, %	K_{20}	K_{25}	K_{30}	K_{35}	K_{30}/K_{20}	K_{35}/K_{25}
0	133.5	210.0	350.2	565.6	2.62	2.69
10	98.8	156.0	268.1	433.5	2.71	2.78
20	71.2	116.0	200.7	337.0	2.82	2.90
30	51.8	88.8	147.8	261.0	2.86	2.94
40	38.5	67.1	111.9	198.6	2.91	2.96
50	28.2	51.6	84.3	154.9	2.98	3.00
60	20.8	38.9	63.7	120.0	3.02	3.08

Discussion of Results

(1) Hydroxide Catalyst.—For the purpose of the present discussion, we shall supplement Bronsted's[3] theory of homogeneous reaction velocity by the inclusion of the term containing the energy of activation of the diacetone alcohol per mole, Q_{12}, and obtain

$$V = km_A m_{OH} \frac{\gamma_A \gamma_{OH}}{\gamma_i} e^{-Q_{12}/RT} \tag{2}$$

m_A and m_{OH} are the concentrations, γ_A and γ_{OH} the activity coefficients of the diacetone alcohol and hydroxide ion, respectively, and γ_i the activity coefficient of the intermediate. At constant temperature, this reduces to Brönsted's equation,

$$V = k'm_A m_{OH} \frac{\gamma_A \gamma_{OH}}{\gamma_i} \tag{3}$$

In dilute solutions the kinetic factor $\gamma_A\gamma_{OH}/\gamma_i$ approaches unity and Equation 3 becomes

$$V = k'm_A m_{OH} \tag{4}$$

That the velocity constant k' is proportional to the hydroxide concentration in the region of concentration from 0.01 to 0.1 molal has been shown by French,[4] and confirmed at all concentrations by the data in the first part of Table I. Since this is the case, the temperature coefficient is independent of the hydroxide concentration, as shown by the velocity constant ratios in the sixth and seventh columns of the table.

At hydroxide concentrations from 0.2 to 6 M, Åkerlöf found that the reaction velocity conformed with that predicted by the equation

$$v = km_A m_{OH} \sqrt{\gamma_M \gamma_{OH}} \tag{5}$$

Since the variation of the activity coefficient with the temperature is small, and probably uniform, we would also expect the temperature coefficient of the reaction velocity to be independent of the hydroxide concentration in the more concentrated solutions.

(2) Hydroxide–Chloride Catalysts.—From the ratios of the velocity

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[3] Bronsted, *Chem. Rev.*, 5, 286 (1928).

[4] French, THIS JOURNAL, 51, 3215 (1929); see also Harned and Åkerlöf, *Trans Faraday Soc.*, *24*, 676 (1928).

constants at different temperatures contained in the last two columns of the second part of Table I, it is clear that the temperature coefficient of the velocity constant is independent of the concentration of the added salt. Further, the mean values of the temperature coefficients are the same as those in the case of the pure hydroxide solutions within the error of the present experimental method.

From these results the value of Q_{12} may be readily computed. Thus, from Equation 2, we find that

$$k = Ae^{-Q_{12}/RT} \tag{6}$$

whence, the equation of Arrhenius

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{Q_{12}}{RT^2} \tag{7}$$

may be obtained by differentiation. Integrating between the limits k_{35} and T_1 and k_{25} and T_2, we obtain

$$\ln\frac{k_{35}}{k_{25}} = \frac{Q_{12}}{R}\,\frac{(T_1 - T_2)}{T_1T_2} \tag{8}$$

Substituting 308.1' for T_1 and 298.1' for T_2 and converting to common logarithms, we find that

$$Q_{12} = 42{,}011 \log\frac{k_{35}}{k_{25}} \tag{9}$$

If we substitute the average values, 2.67 and 2.70, from the last columns of parts (1) and (2) of Table I for k_{35}/k_{25} in this equation, we obtain Q_{12} = 17,918 cal. and Q_{12} = 18,122 cal., respectively. Thus the value of Q_{12} may be taken to be 18,000 cal.

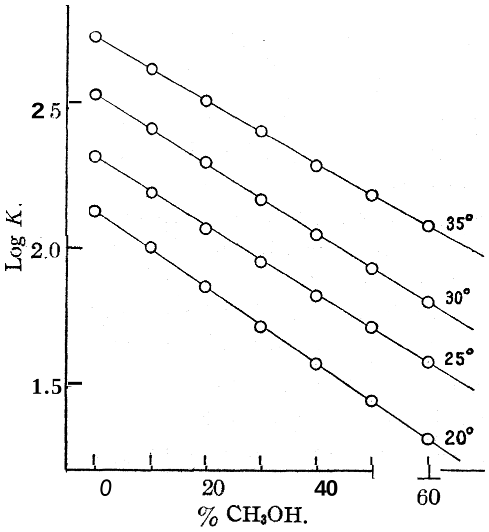

Fig. 1.

(3) Hydroxide Catalyst in Water–Methyl Alcohol **Mixtures.**—The addition of methyl alcohol to the aqueous solution of sodium hydroxide decreases the velocity of decomposition of diacetone alcohol. This was previously shown at 25° by Åkerlöf, who studied the effects of six organic solvent–water mixtures containing sodium hydroxide upon this reaction rate. In Fig. **1** the logarithm of the velocity constants at 20, 25, 30 and 35° contained in the third part of Table I are plotted against the weight percentages of methyl alcohol The plots appear as straight lines up to **a** concentration of 60% alcohol.

It is important to observe, however, that the temperature coefficient is not independent of the methyl alcohol concentration, but that the ratios of the velocity constants at 30 and 20°, and at 35 and 25°, increase with increasing methyl alcohol content, as shown by the sixth and seventh columns of the third part of Table I.

The writer takes this opportunity to thank Professor Herbert S. Harned for help and suggestions obtained from him during the course of this work.

Summary

1. The reaction velocity constant of decomposition of diacetone alcohol catalyzed by hydroxides has been measured at 20, 25, 30 and 35° in aqueous solutions of sodium hydroxide of different concentrations, in aqueous hydroxide–salt solutions, and in water–methyl alcohol mixtures containing sodium hydroxide.

2. The temperature coefficient of reaction velocity is independent of the strength of hydroxide. It is also independent of the sodium chloride concentration in the hydroxide–salt mixtures.

3. The temperature coefficient, however, is not independent of the concentration of methyl alcohol in the alcohol–water mixtures containing 0.1 M sodium hydroxide.

4. The energy of activation has been computed and is found to be 18,000 cal. The error in this observation is approximately ±0.7%.

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

A THEORY OF THE ARRANGEMENT OF PROTONS AND ELECTRONS IN THE ATOMIC NUCLEUS

BY WENDELL M. LATIMER

RECEIVED FEBRUARY 3, 1931 PUBLISHED MARCH 6, 1931

From a study of the number of protons and electrons in those atomic species whose atomic weights are approximately integral multiples of four, together with data on their abundance, I have been led to a geometrical representation of the atomic nuclei in which the protons and electrons are arranged in a definite space lattice. It appears certain that the nucleus must be held together by the coupling of the proton spins, and the model may be interpreted as the pattern determined by the directions of the spin vectors. In the proposed model the angle between any two proton vectors is that formed by lines from two corners of a tetrahedron to its center, and this in the new quantum mechanics is the angle at which two elementary spin vectors add to give a resultant of two units.

It seems reasonable to expect that existing relations would appear more clearly defined in the case of the atomic species with atomic weights multiples of four, since, at least in the lighter elements, these nuclei possess no resultant spin and have therefore a higher degree of symmetry. This nuclear type contains an even number of electrons and thus occurs only in elements of even atomic number with the exception of the two very unstable elements, Mesothorium II with a half life period of six hours, and Thorium c″ with a half period of 3.2 minutes. Every even atomic number from 2 to 90 appears to have at least one atomic species of this type, generally the most abundant form of the element; in fact, approximately 80% of the earth's crust is composed of such atoms.

In analogy to the known facts of radioactive disintegration, it has frequently been suggested[1] that these elements are composed of alpha particles, that is, united of four protons and two electrons, together with that number of extra or "cementing" electrons which, with the number of alpha particles, gives its atomic number. The numbers of these alpha particles and extra electrons are summarized in Table I; the figures in the table are the number of alpha particles for the element with the atomic number given at the left of the same row, and the number of extra electrons in the nucleus is given by the number at the top of the corresponding column.

TABLE I

A REPRESENTATION OF THE NUMBER OF ALPHA PARTICLES AND EXTRA ELECTRONS IN THE NUCLEI OF THE ELEMENTS WITH ATOMIC WEIGHT INTEGRAL MULTIPLES OF FOUR

Element	Atomic number	Number of extra electrons													
		0	2	4	6	8	10	12	14	16	18	20	22	24	26
He	2	1													
Be	4	2													
C	6	3													
O	8	4													
Ne	10	5													
Mg	12	6													
Si	14	7													
S	16	8													
A	18	9	10												
Ca	20	10	11												
Ti	22		12												
Cr	24		13												
Fe	26		14												
Ni	28		15												
Zn	30		16	17											
Ge	32			18											
Se	34			19	20										
Kr	36			20	21										
Sr	38				22										
Zr	40				23										
Mo	42			23	24	25									

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[1] See Harkins, *Chem. Rev.*, 5, 371 (1928), and other papers referred to in this reference.

TABLE I *(Concluded)*

Element	Atomic number	Number of extra electrons													
		0	2	4	6	8	10	12	14	16	18	20	22	24	26
Ru	44				25[a]										
Pd	46					27"									
Cd	48					28	29								
Sn	50					29	30	31							
Te	52							32							
Xe	54					31	32	33							
Ba	56							34							
Ce	58							35							
Nd	60							36							
Sa	62								38[a]						
Gd	64								39"						
Dy	66									41"					
Er	68									42[a]					
Yb	70									43"					
Hf	72										45"				
W	74										46[a]				
Os	76											48"			
Pt	78											49"			
Hg	80											50	51		
Pb	82												52	53	
Po	a4												53	54	
Rn	86													55	
Ra	88													56	
Th	90													57	58
U	92														

[a] From chemical atomic weight and estimated packing fraction. Other values as determined by mass spectrograph.

It is to be observed that the lighter elements may be considered as composed of alpha particles alone, but the maximum number of alpha particles in nuclei of this type is 10, *i.* e., in Calcium, 40. We also find Argon, 40, which contains two extra electrons. Argon **36** and Argon 40 constitute the first example of an element having two isotopes differing in atomic weight by four.

The greatest number of alpha particles found in nuclei which contain two extra electrons is 16 and from this point on the number of extra electrons increases rapidly. Thus, thorium, **232.** the heaviest known member of the class, may be thought of as containing 58 alpha particles and 26 extra electrons. It may also be noted from Table I, that nuclear types containing 6, 12 and 24 extra electrons occur with a large range of atomic weights.

Data on the abundance of the various nuclear species may be expected to give some measure of the relative stabilities of various nuclear structures. In Fig. 1 the abundance, expressed as the logarithm of the percentage of the species in the earth's crust, has been plotted against the number of alpha particles in the various atoms listed in Table I. The data are those given by Harkins[1] for the abundance of the elements, corrected in case the element is a mixture of isotopes, to give the amounts of the element belonging to this nuclear type. Approximate values have been added also for neon and argon. The elements above atomic number 30 constitute but 0.15% of the earth's crust, and as the data regarding their abundance are not reliable the plot has not been extended beyond this point.

These, then, are the facts we wish to correlate with the model, first, that a given number of protons is associated with the number of electrons as given in Table I and, second, that certain groups of protons and electrons appear to be more stable than others as judged by their greater abundance.

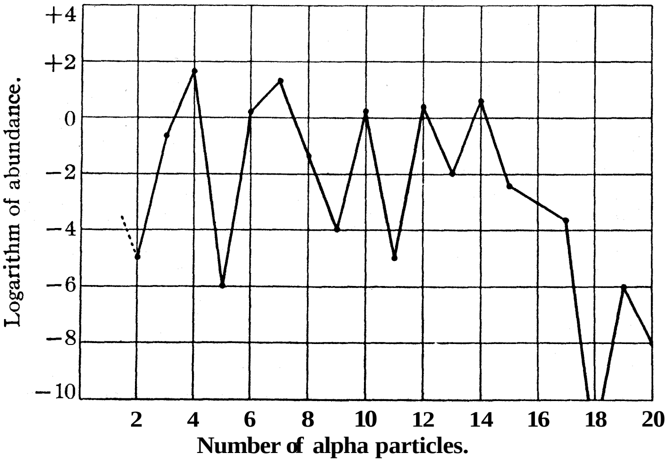

Fig. 1.—The abundance as the log of the percentage of the nuclear species in the earth's crust plotted against the number of alpha particles.

Maxima occur in the abundance curve at 4, 7, 10, 12 and 14 alpha particles. These numbers at once suggest that the alpha particles are combined in a tetrahedral pattern, with one alpha particle at each corner of the unit tetrahedron. Thus, one tetrahedron requires 4 alpha particles; two tetrahedra with one corner in common, seven, and three tetrahedra with a common corner, ten. Such a grouping occurs in face-centered cubic lattice types; the three tetrahedra have their bases in the same plane and share one corner together at the center of the hexagon formed by the outer edges of the base. If we continue this arrangement of tetrahedra, building toward spherical symmetry, we would place a layer of three tetrahedra above the first three as indicated in Fig. 2. With the completion of the first tetrahedron of this new layer we have 12 alpha particles, with the second 14 alpha particles, and with the third 16. Now it appears highly significant that in this arrangement of alpha particles the completion of each of the first five tetrahedra corresponds exactly to the first five maxima of the abundance curve. Moreover, the completion of the first group of three tetrahedra corresponds to the end of the first column of nuclei in Table I, that is, to the nuclei with no extra electrons, and the completion of the second layer of three tetrahedra to the second column of nuclei with two extra electrons. However, to give an explanation of this correspondence it is first necessary to discuss the coupling of the four alpha particles in the unit tetrahedron.

If we represent the alpha particle itself as a tetrahedral arrangement of four protons about an electron pair with zero resultant spin, and assume the four proton spin vectors are directed toward the center of the figure, then the whole alpha particle should have zero spin, in agreement with the experimental facts.[2] Now we wish to group four of these small tetrahedra (alpha particles) into a tetrahedron with such coupling of the spin vectors that a continuation of the pattern will give the arrangement of tetrahedra in Fig. 2. Such a coupling pattern is given in Fig. **3,** which then is to be taken as our model of the oxygen nucleus.

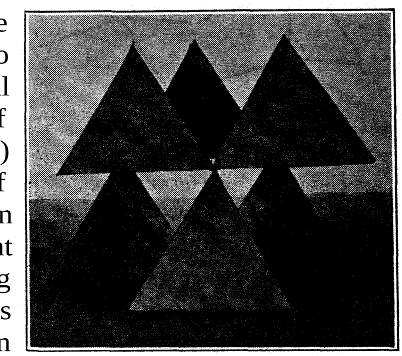

Fig. 2.—Representing the arrangement of 16 alpha particles at the corners of 6 unit tetrahedra.

As the pattern is continued to form the first group of three tetrahedra, we find with the addition of the tenth alpha particle that there is now a point (see A in Fig. 4) about which four spin vectors converge in the same manner as in the unit alpha particle, and it would seem that here too we should have an electron pair. This, then, appears to be an explanation of the entrance of the first pair of extra electrons at 10 alpha particles and provides a basis for the complete interpretation of the number of alpha particles and extra electrons which occur in the atomic nuclei as given in Table I.

[2] I have no doubt that the idea of the probable tetrahedral structure of the alpha particle has suggested itself to many men and it seems to me that this direction of spin vectors is a logical consequence of such a structure. Since preparing this manuscript Dr. O. K. Rice has written that he suggested the idea to me in a conversation a year ago. In the development of the theory I had not recalled his suggestions; however, I have never considered that this postulate regarding the alpha particle was at all original with me.

Several years ago Professor E. D. Eastman of this Laboratory observed that the abundance maxima occurred with a periodicity of 6 atomic numbers in the lighter elements. This observation may now be interpreted in the tetrahedral arrangement of the alpha particles.

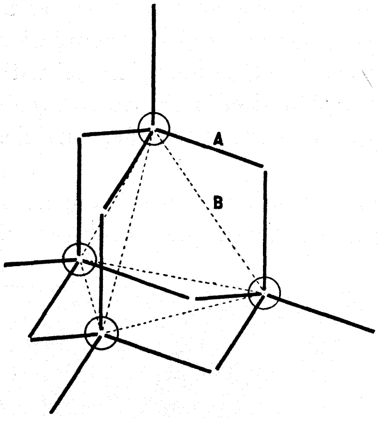

Fig. 3.—The coupling of 4 alpha particles in the unit tetrahedron. Electron pairs located at the positions of the circles and a proton located along each vector.

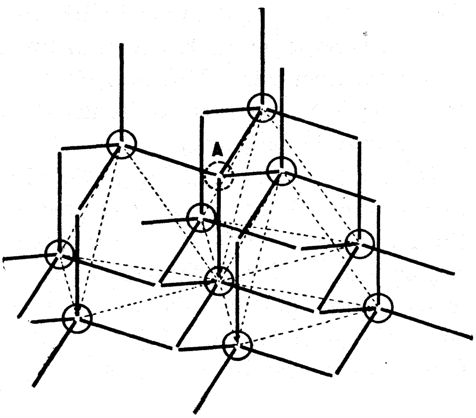

Fig. 4.—The group of 10 alpha particles constituting the first 3 unit tetrahedra. "A" indicates the position of the first pair of extra electrons.

As the pattern, by which the alpha particles are coupled, is continued, it is necessary to add a pair of extra electrons whenever four protons come together at a point and there only. Thus the extra electrons convert the face-centered cubic arrangement of alpha particles into a diamond type lattice of electron pairs, each pair surrounded by four protons which serve as bonds to four other electron pairs. In such a lattice the original alpha particles now appear to have lost their identity. (However, for the sake of clarity in exposition, in all diagrams these extra electron pairs have been represented by black balls, and the electron pairs of the original alpha particles by white balls.)

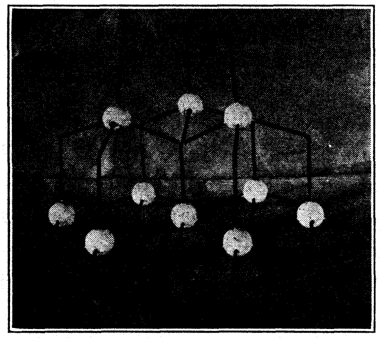

Fig. 5.—A model representing the same group of 10 alpha particles diagrammed in Fig. 4. Electron pairs represented by balls and protons by vectors, *i. e.*, the connecting bars. The model shows the 4 protons coming together at the center.

The method of combining alpha particles is such that it would lead to successive tetrahedra of 20, 35 and 56 alpha particles with 1, 4 and 10 extra electron pairs, respectively. However, the nuclei appear to tend toward spherical form due probably to coulombic forces and a new layer on one of the faces is always started before each of the above tetrahedra is completed, although in each case the figure reaches or approaches very closely the tetrahedra without the corners, that is figures of 16, 31 and 52 alpha particles with the 1, 4 and 10 extra electron pairs. (See Figs. 6, 7 and 8.)

When a new layer is started, one, and then very quickly another electron pair enter and thus we find the groups of electrons, 2 + 4 = 6, 8 + 4 = 12 and 20 + 4 = 24, corresponding, respectively, to the completion of the tetrahedra of 20, 35 and 56 alpha particles and the simultaneous starting of a new layer. This would seem to account for the long columns (see Table I) found with these numbers of extra electrons. Moreover, the evidence seems quite conclusive that when one electron pair goes into a new face, the additional pairs go into the same face of the figure.

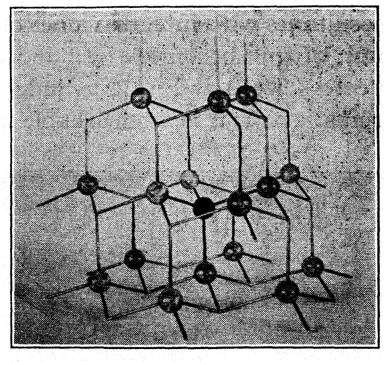

Fig. 6.—The group of 16 alpha particles, with one pair of extra electrons (black ball) at center of figure.

The radioactive thorium series corresponds to the last of these processes of starting a new layer. Thorium, 232, has three extra electron pairs and six alpha particles more than the 52 alpha particle structure of Fig. 8. However, it is not possible to say what should be the most probable location of these additional particles. The end product, lead 208, obviously has one additional pair of electrons in the surface of the 52 alpha particle structure, but again it is not possible to decide whether its alpha particle arrangement is just that of Fig. 8 or some slight variation from it.

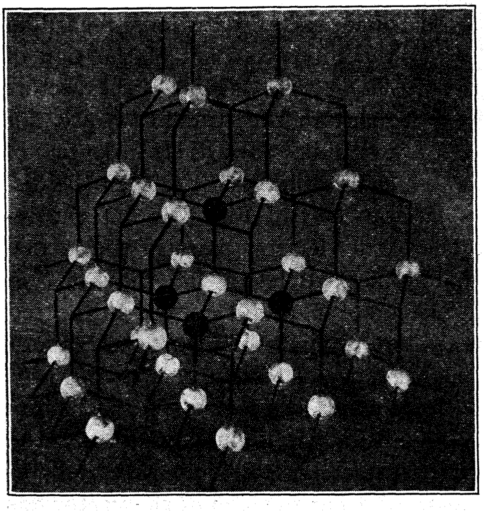

Fig. 7.—The group of 31 alpha particles and 4 pairs of extra electrons.

Although it is not planned to discuss in detail in this paper those elements whose atomic weights are not integral multiples of four, it may be pointed out that the heaviest known stable elements of odd atomic number, bismuth, 209, and thallium, 203, have 10 pairs of extra electrons, as does also lead 206. The latter may correspond to Fig. 8 with two protons removed.

If this proposed nuclear structure is correct in principle, the method of combining the spin vectors certainly should be in agreement with the quantum mechanic rule for vector combination.3 The radical change introduced by the new mechanics is the use of the quantity $\frac{1}{2}\sqrt{n(n+2)}$ as the magnitude of the vector representing n units of spin, and only resultants with integral values of n are permitted. Thus the vector for one unit of spin becomes $\frac{1}{2}\sqrt{3}$ and the only permitted resultants for two such vectors are 0 and $\sqrt{2}$, as judged by the known combinations of electron spins. Now it is a remarkable fact that if the length of the unit vector, **A**, of Fig. **3** is $\frac{1}{2}\sqrt{3}$, then the resultant distance, B, of two such vectors is $\sqrt{2}$. In other words, *the geometry of the tetrahedron is just that demanded by the quantum mechanics for the combination of two unit spin vectors.*

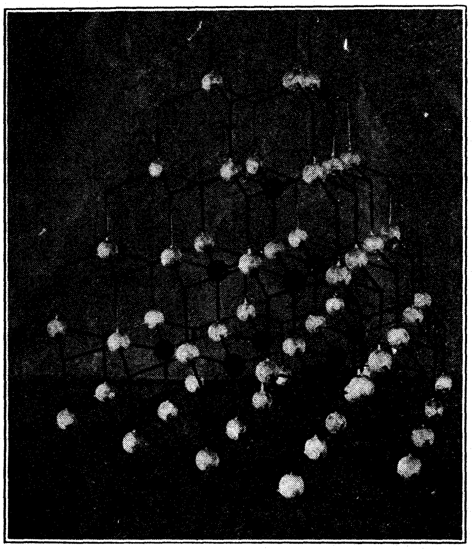

Fig. 8.—Fifty-two alpha particles and 10 pairs of extra electrons.

Unit vectors in two of the directions of the tetrahedron give a resultant of two; unit vectors in three directions, a resultant of one and unit vectors in each of the four directions, a resultant of zero. However, the model at once raises questions regarding the interpretation of the sign of the vectors. Thus if the vectors point in the ordinary sense, for example, toward the center of each alpha particle, then the distance B of Fig. **3** is not the resultant of two unit vectors. Also the extra electron pairs in the lattice would differ from those of the original alpha particles in that the direction of the four spin vectors would be out instead of in, and it might be expected that two kinds of alpha particles and helium atoms would exist corresponding to the two vector forms; yet the existence of the latter appears to be precluded by Lewis' application of the principle of identity to the helium spectrum.[4] However, since in the quantum mechanic vector rule the combination of two unit vectors in the same line can only give zero resultant, the question may be raised as to whether the sign of the vector has meaning in the ordinary sense.

The method of coupling alpha particles leads to a number of cases of

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[3] I am indebted to Professor R. T. Birge for first calling my attention to this requirement.

[4] G. N. Lewis, *Phys. Rev.*, 36, 1144 (1930).

nuclear isomers even among the lighter elements. Thus in Fig. 9, there is given another possible form of calcium 40. This form is not directly obtainable by tearing down the model of Fig. 6, since in that figure the top tetrahedron is not complete; however, if calcium has been formed largely by building up processes rather than by the tearing down of heavier elements, it would seem that this should be an abundant form of the element. This model for calcium minus the four corners gives a very symmetrical form of magnesium, 24.

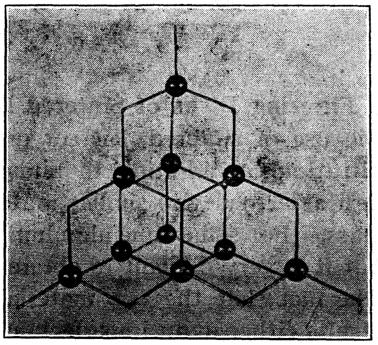

Fig. 9—An isomeric arrangement of 10 alpha particles. Compare Fig. 5.

Although there are numerous other phases of the theory which might be discussed, the author feels that a detailed development should not be undertaken without additional confirmation of the principles involved. It would seem that a study of those elements which have a resultant nuclear spin, may provide this confirmation. For example, if the other types of nuclei are in general derived from those nuclei with weights multiples of four by the removal of one, two or three protons, then the resultant spin should follow at once from the model, provided, of course, that the electrons are all coupled in such a way as to give a zero resultant. However, from the rather meager data we have at present there appears to be some question regarding the validity of this last assumption.

In conclusion the author wishes to express his indebtedness to Professor Gilbert N. Lewis for many valuable suggestions regarding the presentation of the theory.

Summary

An analysis has been made of the nuclear species whose atomic weights are approximately integral multiples of four with reference to the number of alpha particles and extra electrons present.

The abundance curve for the lighter elements of this series shows maxima for 4, **7,** 10, 12 and 14 alpha particles which suggests that the alpha particles are arranged in a tetrahedral pattern.

A pattern is proposed for the arrangement of 4 alpha particles in a tetrahedron with a certain coupling of proton spins. **A** continuation of the pattern to 10 alpha particles leads to a point in the lattice about which four protons converge in the same manner as in the alpha particle. The entrance of a pair of electrons at this point explains the first pair of extra electrons found in argon 40, and an extension of the principle appears

to give a complete explanation of the numbers of extra electrons required in the heavier elements.

With the addition of the extra electrons the proposed nuclear structure becomes a diamond type lattice of electron pairs joined by protons.

The method of coupling proton spins appears to be that demanded by the quantum mechanic rule for vector combination.

BERKELEY, CALIFORNIA

NOTE

Filtering Disks of Sintered Pyrex Glass.—The recent development of the use of sintered Jena or quartz glass disks and alundum plates for filtration, in addition to numerous other applications,[1] makes it very desirable to devise similar material which can readily be fused to pyrex glass. For some time alundum disks have been used in pyrex apparatus, but it is very difficult to obtain a dependable Alundum to pyrex contact. The fact that the two materials have different coefficients of expansion results either in an imperfect junction or in a dangerous strain even after the most careful cooling. The use of sintered pyrex disks would avoid these difficulties. Although these plates are not available from commercial sources, we are able to recommend a procedure whereby a person can, with a little care, prepare for himself satisfactory filtering disks of sintered pyrex.

Scrap pyrex glass crushed to a convenient size is ground to a fairly fine powder either in a pyrex or porcelain mortar or in a grinding machine. The powder is separated into several portions by sifting, *e. g.*: (a) the coarse material which will not pass through a sieve with sixty meshes to the inch, and which should be reground; (b) the part that passes a sixty-mesh sieve, but not an eighty-mesh sieve, and which can be used for making coarse-grained filters; (c) the particles which fall through an eighty-mesh sieve, but do not pass a one hundred-mesh net; (d) the fine powder which is not held by a one hundred-mesh sieve. When a metallic grinding machine is used, the third and especially the fourth portions are contaminated with finely divided metal which gives the disks a grayish cast unless it is removed by acid before sintering.

The apparatus for sintering includes a cylindrical mold, for which we used about one centimeter of nickel tubing with an internal diameter of one centimeter. As indicated in the figure, this cylinder rests on a nickel plate about two and a half centimeters square. The plate may be made large enough to accommodate molds of various sizes if this is desired. In suitable holes drilled at the corners of the plate are fastened nichrome wires arranged to serve both as a handle and as a guide and stay for the

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[1] Prausnitz, *Arch. Pharm.*, 268, 170–184 (1939); *Chem.-Ztg.*, 53, 935–6 (1930).

cover. For this we used a second nickel plate, drilled like the first, sliding it up and down on the wires. A layer of glass powder one and a half to two millimeters thick is then placed in the cylinder and is leveled by gently tapping the container. The cover is put in place and the apparatus is set in a muffle furnace kept at a bright red heat, A little experimentation will give the temperature which gives a sintered disk in about two minutes. If the temperature is too high or the time of sintering too long, a non-porous lump of glass results; if the temperature is too low or the time too short, the disk is weak and friable. The metal of the mold comes to the temperature of the furnace in about a minute, and in the case of the coarse particles of portion (b), another minute is required for satisfactory sintering. The finest powder requires approximately one minute and forty-five seconds from the time the apparatus is put in the furnace. The apparatus is withdrawn from the furnace promptly and is set on a metal plate to cool. The cylinder containing the disk is then removed and inspection shows that, with the two smaller sizes in particular, a slight shrinkage away from the sides of the mold has occurred near the upper part of those disks which are satisfactorily sintered. The disk is quite rugged enough to be pushed out of the mold with a wooden rod. Any uneven places can readily be smoothed down by a file.

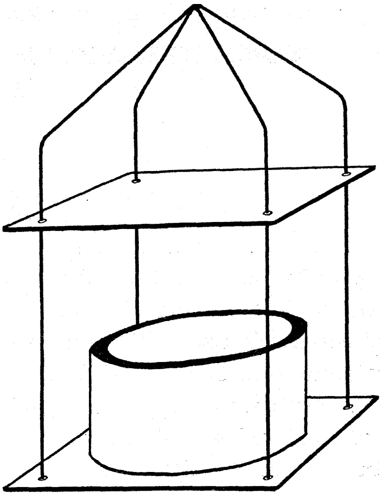

Fig. 1.

For sealing the disks to pyrex apparatus, a pyrex tube of slightly larger diameter than that of the disk is given a slight taper. The disk, inserted in the tube, is supported by the taper and, if necessary, is held straight by a glass rod with a flat end. By careful application of a small hot flame, the disk is attached to the tube at several points. Pushing the hot glass against the side of the disk by means of a nichrome wire may be used to hurry the process. The seal is completed either by rotating the tube in a small hot flame and drawing it down over the disk, or by blowing the glass around the plate in and out in the usual way of making a glass to **glass** seal. A flame of air and gas is preferable to one of oxygen and gas for this purpose.

Disks ten to fifteen millimeters in diameter made according to these directions have been in use for some time and have given entire satisfaction. Those made from particles of portion (b) hold by capillarity a column of mercury ten centimeters high. Filters made from the **fine** powder in portion (d) will hold mercury at half an atmosphere. The sole precaution which we have found necessary is to wrap the filter with asbestos paper if it is to be heated to a high temperature in a vacuum. This protection should also be used to provide slow cooling for a hot filter.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
HARVARD UNIVERSITY
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W. F. BRUCE
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RECEIVED JANUARY 14, 1931
PUBLISHED MARCH 6, 1931

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES, ELI LILLY AND COMPANY]

SOME NEW WATER-SOLUBLE ORGANO-MERCURY COMPOUNDS[1]

BY JOHN H. WALDO

RECEIVED JUNE 16, 1930 PUBLISHED MARCH 6, 1931

Introduction

The application of organo-metallic compounds in the therapeutic field too often has been limited by their insolubility in water. Organic mercury compounds having the mercury attached to a carbon atom have had considerable use in therapy, especially as germicidal agents, although the introduction of the —HgX group into an organic molecule tends to make the resulting compound insoluble in water. When mercury compounds are rendered soluble in water or dilute alkali solutions through the introduction of a sulfonic or carboxylic acid group, they generally become less toxic but undergo a marked reduction in their germicidal activity. However, if nitrogen-containing groups are introduced to give the desired solubility, the germicidal activity is retained, but they are many times more toxic than the group which contains an acid radical.

In 1922, Kharasch[2] developed a method whereby organo-metallic compounds can be made water soluble by condensing them with mercapto-carboxylic or sulfonic acids.

When mercurials of the type RHgX, where X is an inorganic radical, react with a mercapto acid, HSR', where R' is a group containing an alkyl or aryl carboxylic or sulfonic acid, a double decomposition occurs

$$\text{RHgX} + \text{HSR}' = \text{RHgSR}' + \text{HX}$$

The new compound RHgSR' is soluble in sodium bicarbonate solution and forms with the alkali metals soluble salts whose solutions are in general stable and do not give an immediate precipitate of mercuric sulfide with ammonium sulfide.

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[1] A portion of this paper was presented before the division of Medicinal Products at the Detroit meeting of the American Chemical Society, September, 1927, by M. S. Kharasch, H. A. Shonle, and John H. Waldo.

[2] M. S. Kharasch, U. S. Patent 1,589,599, reissue 16,921,

Kharasch and Chalkley[3] showed that variations in the degree of electronegativity of the organic radical will produce a marked effect on the degree of ionization of mercury as evidenced by the readiness with which mercuric sulfide is formed when compounds are treated with hydrogen sulfide or ammonium sulfide. It should therefore be possible to prepare predetermined mercuri-carbon compounds possessing various degrees of lability of the mercury.

The stability of these new compounds depends upon two factors, first, the stability of the R—Hg linkage and second, the S—R' linkage. In regard to the former it could be predicted from the work of Kharasch and Marker,[4] that the higher homologs in the alkyl series would be more stable than the lower members and that aryl groups would be less stable than alkyl or alkaryl groups. Such a prediction proved to be true in this instance. The sulfur atom is quite strongly electronegative and it would therefore be predicted that an electronegative group, such as an aromatic nucleus, attached to it, would tend to produce a greater stability than less electronegative groups, such as those of the straight-chain aliphatic series. Experimental work confirmed this hypothesis.

Experimental Part

Preparation of Organo Mercury Halides.—The various alkyl and aryl mercury halides used in this investigation were prepared by the Grignard reaction. In carrying out these reactions, two reflux systems were used, designed to filter the Grignard reagent without contact with air. The flask containing mercuric chloride in ether was connected by a glass tube extending to the bottom of the Grignard reaction flask. At the completion of the original reaction the Grignard reagent was forced into the second flask by compressed air. The end of the connecting tube was covered with 200-mesh silk bolting cloth to act as a filter.

Preparation of Mercapto Acids.—All of the rnercapto acids used in this investigation have been described previously in the literature. Two general methods were used, the first according to Schacht and of Duvillier,[5] which consisted in treating the desired aliphatic halogen substituted acids with potassium hydrogen sulfide in alcohol solution; and the second as outlined by Leuchart,[6] which involves the formation of the xanthogen ester, by treating the desired diazonium salt with potassium ethyl xanthate. This hydrolyzed to the mercapto acid in about 60–70% yield. If, however, the initial precipitate of the crude acid is dissolved in excess alkali and reduced by boiling with zinc dust, the yield is frequently increased to 90%.

Preparation of the Salts of Organo Mercuri-mercapto Acids.—As

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[3] M. S. Kharasch and L. Chalkley, Jr., THIS JOURNAL, 46, 1211 (1924).

[4] M. S. Kharasch and R. Marker, *ibid.*, 48, 3130 (1926).

[5] C. Schacht, *Ann.*, 129, 1 (1864); E. Duvillier, *Bull. soc. chim.*, 30, 507 (1878).

[6] R. Leuchart, *J. prakt. Chem.*, [II] 41, 179 (1890).

indicated above, the condensation of organo mercury salts with the mercapto acids proceeds very quickly and smoothly in a dilute alcoholic sodium hydroxide solution.

In carrying out the synthesis it was more convenient to use two moles of alkali instead of one, thus initially obtaining the water-soluble sodium salt. The water-insoluble acids are precipitated by acidification and purified by crystallization from alcohol or acetone.

Methyl Mercurithiosalicylic Acid, (o-$CH_3HgSC_6H_4COOH$).—Forty grams of methyl mercuric iodide (0.12 mole) is moistened with 20–30 cc. of 95% ethyl alcohol and to this is added 96 cc. of 10% sodium hydroxide solution (0.24 mole). This solution is then added to a 95% ethyl alcohol solution of 18 g. of thiosalicylic acid (0.12 mole). The solution is filtered, and methylmercurithiosalicylic acid precipitates by acidification with 10% sulfuric acid. Crystallization from 50 cc. of 95% ethyl alcohol gives an 80–85% yield. It is a white crystalline compound melting at 174°,[7] soluble in alcohol, ether and acetone, but insoluble in water and acid.

Anal. Subs., 0.2237: CO_2, 0.2135; H_2O, 0.0408. Calcd. for $C_8H_8O_2SHg$: C, 26.09; H, 2.17. Found: C, 26.01; H, 2.03. Subs., 0.2500: 13.2 cc. of N/10 KSCN. Calcd.: Hg, 54.34. Found: Hg, 52.95.

Ethyl Mercurithiosalicylic Acid, (o-$C_2H_5HgSC_6H_4COOH$).—Ethyl mercuric chloride and thiosalicylic acid are combined by an identical method, giving a white crystalline solid melting at 111°.

Anal. Subs., 0.2950: CO_2, 0.3077; H_2O, 0.0714. Calcd. for $C_9H_{10}O_2SHg$: C, 28.27; H, 2.63. Found: C, 28.40; H, 2.68. Subs., 0.2000: 10.45 cc. of N/10 KSCN. Calcd.: Hg, 52.41. Found: Hg, 52.40.

p-Ethyl Mercuri-mercaptobenzoic Acid, (p-$C_2H_5HgSC_6H_4COOH$).—Ethylmercuric chloride and p-mercaptobenzoic acid are combined by an identical method giving a white crystalline solid which does not melt up to 250°.

Anal. Subs., 0.2570: CO_2, 0.2718; H_2O, 0.0575. Calcd. for $C_9H_{10}O_2SHg$: C, 28.27; H, 2.63 Found: C, 28.84: H, 2.49. Subs., 0.3000: 15.6, 15.8 cc of N/10 KSCN. Calcd.: Hg, 52.41. Found: Hg, 52.14, 52.82.

Isoamyl Mercurithiosalicylic Acid, (o-iso-$C_5H_{11}HgSC_6H_4COOH$).—Isoamyl mercuric chloride and thiosalicylic acid are combined by an identical method giving a white crystalline solid melting at 78°.

Anal. Subs, 0.2720: CO_2, 0.3321; H_2O, 0.0883. Calcd. for $C_{12}H_{16}O_2SHg$: C, 33.95; H, 3.77. Found C, 33.30; H, 3.60. Subs., 0.3000: 14.25 cc. of N/10 KSCN. Calcd.: Hg, 47.19. Found: Hg, 47.63.

Several additional products were made, but due to small amounts of reagents low yields were obtained. It seemed more desirable to ascertain their germicidal value and sacrifice a complete chemical analysis. There-

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[7] All melting points taken with a standardized thermometer and corrected for stem exposure

fore, only mercury assays were made. In view of the fact, however, that identical methods were used and that they were purified by crystallization to constant melting points, it is reasonable to assume the structure of all is the same.

TABLE I

COMPOUNDS, CONSTANTS AND ANALYTICAL DATA

Acid, ( ) = mercuri	M. p., °C.	Formula	Metcury analyses, % Calcd.	Found	
Phenyl ()-thiosalicylic	228.5 (dec.)	$C_{13}H_{10}O_2SHg$	46.57	46.63	46.79
Benzyl ()-thiosalicylic	144.5 (dec.)	$C_{14}H_{12}O_2SHg$	45.04	45 12	44.95
a-Ethyl ()-mercaptobutyric	76	$C_6H_{12}O_2SHg$	57.47	56.66	
p-Ethyl ()-mercaptophenylacetic	116.7	$C_{10}H_{12}O_2SHg$	50.50	50.30	50.39
p-Ethyl ()-mercaptobenzenesulfonic	Above 300	$C_8H_{10}O_3S_2Hg$	47.84	46.67	

All compounds are white crystalline solids. Mercury analyses by the potassium thiocyanate method.

p-Ethyl Mercuri-mercaptobenzenesulfonic Acid, (*p*-$C_2H_5HgSC_6H_4$-SO_3H.—Five grams of ethyl mercuric chloride dissolved in 20–30 cc. of warm 95% ethyl alcohol is added to 3.6 g. of *p*-mercaptobenzenesulfonic acid in an equal volume of alcohol. A precipitate starts forming in a few minutes. After standing for two to three hours at room temperature, the precipitate is recovered and dried.

Discussion

It is not the purpose of this paper to outline any bacteriological test. However, some indication of the change in toxicity and germicidal effect may be obtained from an examination of the values for the sodium salts of the above compounds. Disregarding other factors, the best germicide in any series should combine the lowest toxicity with the highest bactericidal value. A therapeutic index may be obtained by the product of these values, and if sodium ethyl mercurithiosalicylate be given the value one, a representative ratio of indices is given. The germicidal values were obtained by a slight modification of the technique outlined by Reddish,[8] by using undiluted horse serum for the diluent. The data and therapeutic index are given in Table II.

The table indicates that the alkaryl mercuri derivatives are less toxic than the aryl, that salts of carboxylic acids are less toxic than sulfonic acids, that some decrease in the index is produced by a change from the ortho to the para position on the benzene ring,[9] and by alkyl instead of alkaryl derivatives. Further, it has been observed that alkyl compounds are decidedly less stable, either in solution or dry than alkaryl products.

The benzyl mercurithiosalicylic acid described above was not obtained in sufficient quantity to obtain authentic figures on toxicity, but its germi-

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[8] G. F. Reddish, Am. J. Pub. *Health*, 17, 320–329 (1927).

[9] The meta derivative, which has been prepared in about 94% purity, gives data in agreement with this conclusion

TABLE II

THERAPEUTIC INDICES

Compounds	Toxicity to rats, M. L. D. in mg. per kg.	Bactericidal dilutions *B. typhosus*	*Staph. Aureus*	Index *B. Typhosus*	*Staph. Aureus*
o-$CH_3HgSC_6H_4COONa$	40	1–2000	1–4000	0.533	0.80
o-$C_2H_5HgSC_6H_4COONa$	50	1–3000	1–4000	1.0	1.0
o-$C_5H_{11}HgSC_6H_4COONa$	60	1–2000	1–3000	0.80	0.90
o-$C_6H_5HgSC_6H_4COONa$	15	1–1000	1–1000	.10	.075
p-$C_2H_5HgSC_6H_4COONa$	100	1–1000	1–1000	.667	.50
p-$C_2H_5HgSC_6H_4CH_2COONa$	100	1–1000	1–2000	.667	1.0
$C_2H_5HgSCH(COONa)CH_2CH_3$	80	1–1000	1–1000	.533	0.40
p-$C_2H_5HgSC_6H_4SO_3Na$	25	1–1000	1–1000	.167	.125

cidal values were sufficiently low to indicate the influence of the aryl group on toxicity and its probable low index.

The writer is indebted to Dr. G. H. A. Clowes and H. A. Shonle for many suggestions connected with the preparation of these compounds and to R. M. Lingle for the mercury assays.

Summary

1. Nine new organo-mercury compounds have been prepared.
2. In water solution their sodium salts are desirable germicides.
3. A therapeutic index indicates that an alkaryl combination is the most stable and germicidal type.

INDIANAPOLIS, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. VI

BY C. B. POLLARD AND R. E. NELSON

RECEIVED AUGUST 1, 1930 PUBLISHED MARCH 6, 1931

When diacyl derivatives of o-aminophenol were prepared in the past by the usual methods, it was found in most cases that the order of introduction of the two different acyl groups has no influence upon the formation of the diacyl, identical products being isolated from the two acylations. The position of the acyl groups of the molecule can be determined by removing the group attached to the oxygen by saponification with dilute alkali, and determining from the physical constants of the remaining monoacylated product the group attached to the nitrogen. The identical diacyls mentioned above were found to saponify to yield identical products, as would be expected.

The formation of identical rather than isomeric products on reversing the order of acylation indicates that during acylation a rearrangement must have occurred in one of the two cases. It has been found that certain acyl groups have more power than others to bring about this migration, weight and acidity of the group being considered to have the predominating influence in their obtaining a position in the more basic amino group in preference to the phenol group.

Previous work on this subject by Ransom,[1] Ransom and Nelson,[2] Nelson and others,[3] and Raiford and others[4] is discussed in the literature.

In view of the experimental evidence that relative acidity and weight of the acyl groups play some role in these rearrangements, this investigation was an attempt to determine the effects of these factors when one of the acyl groups was a constant throughout the experiments. Phenylacetyl chloride was used as one of the acylating agents in the preparation of all diacyl derivatives of o-aminophenol in these experiments. The selection of the phenylacetyl group afforded the use of lighter and heavier acyl groups and acyl groups derived from weaker and stronger acids.

When o-phenylacetylaminophenol was acylated with acetyl chloride, a diacyl melting at 101–102° was produced, while the acylation of o-acetylaminophenol with phenylacetyl chloride gave a diacyl melting at 99–100°. A mixture of these two diacyls melted at 76–79°, showing the two to be different. Saponification of each of these diacyls produced only *o*-phenylacetylaminophenol, indicating that in the latter case migration of the phenylacetyl group from the oxygen to the nitrogen must have occurred. Similar results were obtained with diacyls containing the propionyl and chloroacetyl groups. The saponification of these isomers involved rearrangements in which the phenylacetyl group replaced the lighter and less acidic acetyl and propionyl groups and the lighter and more acidic chloroacetyl group.

o-Phenylacetylaminophenol acylated with n-butyryl chloride gave *o*-phenylacetylaminophenyl *n*-butyrate, which yielded *o*-phenylacetylaminophenol on saponification. Acylation of o-n-butyrylaminophenol with phenylacetyl chloride produced o-n-butyrylaminophenyl phenylacetate. Saponification of this diacyl gave o-n-butyrylaminophenol. A rearrangement did not occur in either case. In the first case the phenylacetyl group, which is the heavier and more acidic group, is attached while in the second case the lighter and less acidic n-butyryl group is attached to the nitrogen. Similar results were obtained with diacyls containing the benzoyl group, which is lighter and more acidic than the phenylacetyl group.

Acylation of o-phenylacetylaminophenol with *n*-valeric anhydride gave

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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) 49, 3129 (1927); (d) 50, 919 (1928); (e) 51, 2761 (1929).

[4] (a) Raiford and others, *ibid.*, 41, 2068 (1919); (b) 44, 1792 (1922); (c) 45, 469 (1923); (d) 45, 1728 (1923); (e) 44 430 (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).

o-phenylacetylaminophenyl n-valerate. Saponification of this diacyl produced crystals melting from 94–99° which when mixed with *o*-phenylacetylaminophenol (m. p. 149–150°) melted from 102–120°. When mixed with o-n-valerylaminophenol (m. p. 78.5–79.5°), the mixture melted from 72–75°. Mixtures of the two possible pure monoacyls were made; such a mixture of approximately 65% o-phenylacetylaminophenol and 35% o-n-valerylaminophenol melted from 93–98°. Some of the saponification product was added to this mixture of the pure monoacyls and the resulting mixture melted through practically the same range. Evidently the saponification product was about 65% *o*-phenylacetylaminophenol and 35% o-n-valerylaminophenol, showing that a partial rearrangement occurred. When o-n-valerylaminophenol was acylated with phenylacetyl chloride, o-n-valerylaminophenyl phenylacetate was produced. Saponification of this diacyl gave only *o*-*n*-valerylaminophenol, a rearrangement did not occur and the lighter and less acidic valeryl group was attached to the nitrogen atom.

When o-phenylacetylaminophenol was acylated with isovaleryl chloride, o-phenylacetylaminophenyl isovalerate was formed, while the introduction of the acyl groups in reverse order gave the isomeric diacyl *o*-isovalerylaminophenyl phenylacetate. Saponification of each of these diacyls produced o-isovalerylaminophenol. In the first case the isovaleryl radical, which is the lighter and less acidic radical, migrated from the oxygen to the nitrogen.

Acylation of o-phenylacetylaminophenol with m-chlorobenzoyl chloride gave o-phenylacetylaminophenyl m-chlorobenzoate. Introduction of the acyl group in reverse order gave *o*-(*m*-chlorobenzoylamino)-phenyl phenylacetate. Each of these diacyls gave m-chlorobenzoylaminophenol on saponification. A migration of the m-chlorobenzoyl group, which is the heavier and more acidic radical, from the oxygen to the nitrogen occurred during saponification of the first diacyl.

The acylation of *o*-(*m*-bromobenzoylamino)-phenol with phenylacetyl chloride produced *o*-(*m*-bromobenzoylamino)-phenyl phenylacetate. On saponification this diacyl gave *o*-(*m*-bromobenzoylamino)-phenol. Attempts to prepare this diacyl or its isomer by introducing the acyls in reverse order were unsuccessful.

When o-phenylacetylaminophenol was acylated with methyl chlorocarbonate, the same diacyl was produced as when methyl *o*-hydroxycarbanilate was acylated with phenylacetyl chloride. Saponification of this diacyl yielded a mixture of approximately 50% of each of the two possible monoacyls. A partial rearrangement occurred during saponification or the diacyl was an equilibrium mixture of the two possible diacyls. The latter does not seem probable, as the diacyl melted at 105–106°.

When o-phenylacetylaminophenol was acylated with ethyl chlorocarbonate, the same diacyl was obtained as when ethyl o-hydroxycarbanilate was acylated with phenylacetyl chloride, Saponification gave ethyl *o*-hydroxycarbanilate, showing the carboethoxy group to be attached to the nitrogen.

Acylation of *o*-phenylacetylaminophenol with isobutyl chlorocarbonate gave the same diacyl as when isobutyl o-hydroxycarbanilate was acylated with phenylacetyl chloride. Saponification showed the isocarbobutoxy group attached to the nitrogen.

Experimental

All monoacyls were prepared by the method of Groenvik[6] using *o*-aminophenol and the acid chloride. Their properties are summarized in Table I.

TABLE I

PROPERTIES OF MONOACYLS

Phenol	Formula	M. p., °C.	Yield, %	Analyses, N, % Calcd.	Found
o-Phenylacetylamino-	$HOC_6H_4NHCOCH_2C_6H_5$	149–150	60	6.16	6.21
o-*n*-Butyrylamino-	$HOC_6H_4NHCOC_3H_7$	80–81	58	7.81	7.62
o-(*m*-Bromobenzoylamino)-	$HOC_6H_4NHCOC_6H_4Br$	180	60	4.79	4.86
o-(*m*-Chlorobenzoylamino)-	$HOC_6H_4NHCOC_6H_4Cl$	156–158	52	5.64	5.51

The other monoacyls used, which have been described previously, were made by the same method.

o-Phenylacetylaminophenyl Acetate ($C_6H_5CH_2CONHC_6H_4OCOCH_3$).—To 3 g. of o-phenylacetylaminophenol a slight excess (1.4 g.) of acetyl chloride was added. After the addition of a drop of sulfuric acid, the mixture was stirred and heated on the water-bath for thirty minutes. A purplish-black oil formed which solidified when cold water was added. The solid was finely ground and washed with warm water. It was then dissolved in hot dilute alcohol, filtered and crystallized as flesh-colored, light flaky crystals. Repeated crystallizations gave crystals melting at 101–102°.

About 1 g. of this compound was saponified in the equivalent quantity of 10% potassium hydroxide. After complete solution resulted, the solution was acidified with dilute hydrochloric acid. A yellowish-brown precipitate formed which was washed with warm water and crystallized from dilute alcohol. These crystals melted at 147.5–148.5° and when mixed with o-phenylacetylaminophenol (m. p. 148–149°) melted at 148–149°, showing them to be identical.

o-Acetylaminophenyl Phenylacetate ($CH_3CONHC_6H_4OCOCH_2C_6H_5$).—A slight excess (3.2 g.) of phenylacetyl chloride was added to 3 g. of o-acetylaminophenol. A drop of sulfuric acid was added, the mixture stirred and heated on the water-bath for thirty minutes. A dark blue oil formed which solidified on addition of cold water. The solid was ground fine, washed with warm water and dissolved in hot dilute alcohol. On cooling it crystallized as pinkish-brown flakes. After four crystallizations the melting point was constant at 99–100°. Some of these crystals were mixed with the diacyl made in the reverse order and the mixture melted from 76–79", showing the two to be different.

This diacyl was saponified in the same manner as the preceding one and yielded *o*-phenylacetylaminophenol. A rearrangement must have occurred during saponification.

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[6] Groenvik, Bull. *soc. chim.,* [2] 25, 173 (1876).

TABLE II

DIACYL DERIVATIVES OF *o*-AMINOPHENOL

	Name	Formula	M. p. °C	Yield, %	Analyses, N, % Calcd.	Found	Saponification product
1	o-Phenylacetylaminophenyl acetate	$C_6H_5CH_2CONHC_6H_4OCOCH_3$	101–102	60	5.20	5.50	$C_6H_5CH_2CONHC_6H_4OH$
2	o-Acetylaminophenyl phenylacetate	$CH_3CONHC_6H_4OCOCH_2C_6H_5$	99–100	45	5.20	5.40	$C_6H_5CH_2CONHC_6H_4OH$
3	o-Phenylacetylaminophenyl propionate	$C_6H_5CH_2CONHC_6H_4OCOC_2H_5$	98-99	40	4.94	4.74	$C_6H_5CH_2CONHC_6H_4OH$
4	o-Propionylaminophenyl phenylacetate	$C_2H_5CONHC_6H_4OCOCH_2C_6H_5$	71–72	35	4.94	4.76	$C_6H_5CH_2CONHC_6H_4OH$
5	o-Phenylacetylaminophenyl butyrate	$C_6H_5CH_2CONHC_6H_4OCOC_3H_7$	91–92	40	4.71	4.52	$C_6H_5CH_2CONHC_6H_4OH$
6	*o*-*n*-Butyrylaminophenyl phenylacetate	$C_3H_7CONHC_6H_4OCOCH_2C_6H_5$	4648	40	4.71	4.57	$C_3H_7CONHC_6H_4OH$
7	o-Phenylacetylaminophenyl valerate	$C_6H_5CH_2CONHC_6H_4OCOC_4H_9$	80–82	50	450	4.60	65% $C_6H_5CH_2CONHC_6H_4OH$ 35% $C_4H_9CONHC_6H_4OH$
8	o-n-Valerylaminophenyl phenylacetate	$C_4H_9CONHC_6H_4OCOCH_2C_6H_5$	71–72	40	4 50	4.39	$C_4H_9CONHC_6H_4OH$
9	o-Phenylacetylaminophenyl isovalerate	$C_6H_5CH_2CONHC_6H_4OCOC_4H_9$	87–88	50	4.50	4.31	Iso-$C_4H_9CONHC_6H_4OH$
10	o-Isovalerylaminophenyl phenylacetate	$C_4H_9CONHC_6H_4OCOCH_2C_6H_5$	56–57	55	4.50	4.28	Iso-$C_4H_9CONHC_6H_4OH$
11	o-Phenylacetylaminophenyl monochloroacetate	$C_6H_5CH_2CONHC_6H_4OCOCH_2Cl$	106–107	50	4.61	4.86	$C_6H_5CH_2CONHC_6H_4OH$
12	o-Monochloroacetylaminophenyl phenylacetate	$ClCH_2CONHC_6H_4OCOCH_2C_6H_5$	113–114	55	4.61	4.82	$C_6H_5CH_2CONHC_6H_4OH$
13	o-Phenylacetylaminophenyl benzoate	$C_6H_5CH_2CONHC_6H_4OCOC_6H_5$	110–111	60	4.23	4.08	$C_6H_5CH_2CONHC_6H_4OH$
14	o-Benzoylaminophenyl phenylacetate	$C_6H_5CONHC_6H_4OCOCH_2C_6H_5$	108–109	75	4.23	4.10	$C_6H_5CONHC_6H_4OH$
15	*o*-Phenylacetylaminophenyl m-chlorobenzoate	$C_6H_5CH_2CONHC_6H_4OCOC_6H_4Cl$	146–148	65	3.82	3.64	$ClC_6H_4CONHC_6H_4OH$
16	*o*-(*m*-Chlorobenzoylamino)phenyl phenylacetate	$ClC_6H_4CONHC_6H_4OCOCH_2C_6H_5$	150–152	55	3.82	3.92	$ClC_6H_4CONHC_6H_4OH$
17	o-Phenylacetylaminophenyl *m*-bromobenzoate	$C_6H_5CH_2CONHC_6H_4OCOC_6H_4Br$	Several attempts failed to produce this compound				
18	*o*-(*m*-Bromobenzoylamino)phenyl phenylacetate	$BrC_6H_4CONHC_6H_4OCOCH_2C_6H_5$	157–159	55	3.41	3.48	$BrC_6H_4CONHC_6H_4OH$
19	Phenylacetate of methyl o-hydroxycarbanilate	$C_6H_5CH_2COOC_6H_4NHCOOCH_3$	105–106	60	4.91	4.85	50% $C_6H_5CH_2CONHC_6H_4OH$ 50% $CH_3OCONHC_6H_4OH$
20	Phenylacetate of ethyl o-hydroxycarbanilate	$C_6H_5CH_2COOC_6H_4NHCOOC_2H_5$	62-63	40	4.68	4.58	$C_2H_5OCONHC_6H_4OH$
21	Phenylacetate of isobutyl o-hydroxycarbanilate	$C_6H_5CH_2COOC_6H_4NHCOOC_4H_9$	72–73	53	4.28	4.25	Iso-$C_4H_9OCONHC_6H_4OH$

All diacyl derivatives of o-aminophenol except the phenylacetates of methyl, ethyl and isobutyl o-hydroxycarbanilate were made by the method described above using the monoacyl, the acid chloride and a drop of sulfuric acid, which is a modification of the method of Jacobs, Heidelberger and Rolf or by the method of Jacobs, Heidelberger and Rolf[6] using the monoacyl, the acid anhydride and a drop of sulfuric acid. The *o*-hydroxycarbanilates were made by the Schotten–Baumann reaction. The properties of all of these diacyls are summarized in Table II.

The melting points in the cases of three pairs of isomers listed above as 1, 2, 13, 14, 15 and 16 might indicate the possibility that in each case they were identical substances in an impure state, but the facts that each substance appeared to be homogeneous and the melting points of the mixtures were decidedly lower lead to the conclusion that they were isomers.

Mixed melting point of 1 and 2	76–79"
Mixed melting point of 13 and 14	80–90°
Mixed melting point of 15 and 16	128–135°

Summary

A study of the diacyl derivatives of o-aminophenol, when one of the acyl groups was always the phenylacetyl radical, has been made. The phenylacetyl group was checked against the acetyl, propionyl, butyryl, valeryl, isovaleryl, monochloroacetyl, benzoyl, m-chlorobenzoyl, *m*-bromobenzoyl, carbomethoxy, carboethoxy and isocarbobutoxy groups.

When both acylating agents were of the type (ClCOR), isomeric diacyls were obtained depending on the order of introduction of the acyl groups. In five cases out of eight complete rearrangement occurred during saponification, one case showed partial rearrangement and in two rases rearrangement did not occur.

Apparently relative acidity and weight are not the controlling factors in this type of rearrangement. Where complete rearrangement did occur the nitrogen atom was shown to be attached to the heavier and more acidic group in three cases, to the heavier and less acidic in one case and to the lighter and less acidic in another. Although there were differences in weight and acidity of the acyl groups, one case showed only partial rearrangement and two cases showed no migration of the acyl groups even during saponification.

Where one of the acylating agents was an alkyl chlorocarbonate (ClCOOR), the same diacyl derivative was obtained regardless of the order of introduction of the groups. Saponification of these diacyls gave a mixture of the two possible monoacyls in one case and showed no migration of the groups in the other two cases. In the last two cases the phenylacetyl group was removed by saponification, showing it to be attached to the oxygen in the diacyls.

New mono and diacyl derivatives of o-aminophenol have been made and studied.

LAFAYETTE, INDIANA

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[6] Jacobs. Heidelberger and Rolf, THIS JOURNAL. 41,458 (1919).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OB THE UNIVERSITY OF TEXAS]

THE NITROGEN COMPOUNDS IN PETROLEUM DISTILLATES. III. THE STRUCTURE OF A HYDROAROMATIC BASE OF THE FORMULA $C_{16}H_{25}N$[1]

BY W. C. THOMPSON[2] AND J. R. BAILEY[3]

RECEIVED AUGUST 8, 1930 PUBLISHED MARCH 6, 1931

Introduction

Recently there was published from the Texas Laboratory a paper entitled "An Investigation of the Bases in the Kerosene Distillate of California Petroleum."[4]

This work has been continued in an attempt to establish the structural formula of a *hydroaromatic* base of the formula, $C_{16}H_{25}N$, and the reader is referred to the paper cited for detailed information on the procedure followed in its isolation.[5] It is obvious that the structural problems involved here are comparable to those in alkaloidal chemistry; as a matter of fact, were it of plant occurrence, the $C_{16}H_{25}N$ compound would undoubtedly be termed an alkaloid. Since hydroaromatic bases, in contrast to those of aromatic types, predominate in petroleum distillates,[6] it might seem appropriate to give the hydroaromatic types the class name, "*Petroleum Alkaloids*."[7] While it is true that the so-called petroleum bases,

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[1] This paper contains results obtained at the Chemical Laboratory, University of Texas, in an investigation on "The Nitrogen Compounds in Petroleum," listed as Project **20** of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Junior Research Fellow.

[3] Director American Petroleum Institute Project 20.

[4] Poth, Schulze, King, Thompson, Slagle, Floyd and Bailey, THIS JOURNAL, 52, **1239 (1930).**

[5] Our supply of crude kerosene bases was extracted from **150** barrels of the residue obtained at the Oleum Plant of the Union Oil Company of California in refining their crude kerosene stock with liquid sulfur dioxide. In the paper cited, p. **1242,** this material is referred to as "probably the largest amount of so-called petroleum bases ever assembled for investigation."

Mr. H. K. Ihrig of Pittsburgh, Penna., recently informed one of the authors that during **1926–1927,** in an investigation financed by the Associated Oil Company, he isolated **1100** gallons of base from **10,000** barrels of Edeleanu extract. U. S. patents, **1,671,721** (5/29/28), and **1,686,136** (10/2/28), assigned "one-half to S. E. Campbell of Associated, California, and one-half to Associated Oil Company, of San Francisco," were an outgrowth of this work.

[6] On the suspected presence of hydroaromatic bases in coal-tar distillates, *cf.* J. von Braun, **Ann,** 478, **182 (1930);** Decker and **Dunant, Ber.,** 42, **1178 (1903).**

[7] Prof. Austin M. Patterson, to whom the authors are indebted for valuable suggestions in connection with problems of nomenclature presented in this paper, writes:

unlike the most important plant alkaloids, are oxygen-free, there are also oxygen-free plant alkaloids, such as coniine and nicotine. Furthermore, it may be expected that further study of the bases in petroleum distillates will reveal hydroaromatic types containing the *pyrrole* nucleus and a closer analogy be thus established. Whether any of the basic substances formed in the distillation of petroleum will ever attain a pharmacological importance at all comparable to that of plant alkaloids presents a question that cannot be answered at this time.[8]

Developments in connection with A. P. I. Project 20, as well as investigations elsewhere, indicate conclusively that hydroaromatic bases in great numbers and of various types, along with aromatic bases,[9] exist in all unrefined, California, petroleum distillates. The procedure being employed in the Texas Laboratory for the isolation of so-called petroleum bases, and for the perfection of which Research Fellow, E. J. Poth, deserves a large share of credit, involves the successive employment of: (1) dilute sulfuric acid extraction; (2) exhaustive fractional distillation; **(3)** resolution with buffered acid solutions; and (4) recrystallization of appropriate salts. In this way both types of bases, in contrast to the non-reactive, associated hydrocarbons, can be isolated free of admixtures.

The $C_{16}H_{25}N$ base shows an unusual stability toward permanganate in both neutral and alkaline solution but is quite readily attacked in acid solution. However, it is very resistant to oxidation with chromic acid in sulfuric acid solution. Heated with fuming sulfuric acid, it is oxidized with a violent evolution of sulfur dioxide just above 200°, but the reactions involved have not been studied. After numerous preliminary experiments

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"These hydroaromatic bases are like plant alkaloids in structure and the term, alkaloid, has been used for organic bases of non-vegetable origin; still, the tendency in recent times has been to restrict it to plant bases." On prior use of phrase "petroleum alkaloids," cf. **A.** Weller, *Ber.*, 20, 2098 (1887); F. X. Bandrowski, *Monatsh.*, 8,224 (1887).

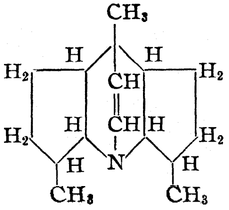
[8] A report on physiological tests, carried out on dogs and guinea pigs with the hydrochloride of the $C_{16}H_{25}N$ base, by Dr. E. J. Poth of Johns Hopkins University is submitted: "It is of low toxicity. Upon intravenous administration to anesthetized animals, the blood pressure and heart-rate are not altered and there is no action on bronchial musculature. However, there is a low-grade irritant action, from which recovery is slow, on isolated strips of virgin guinea pig's uterus. The substance was not further investigated."

As an indication of the importance petroleum bases may assume, the following communication from Dr. Erich Hesse, Professor of Pharmacology and Experimental Therapy in the University of Breslau, Breslau, Germany, is of interest: "I am anxious to examine the different fractions of your crude bases in their action on tubercular bacilli. Strong evidence warrants the forecast of anti-bacterial, active constituents among the kerosene bases."

[9] King and Bailey obtained 2,3,8-trimethylquinoline from the distillation fraction where the $C_{16}H_{25}N$ base occurs and proved its structure by synthesis (Ref. 4, p. 1245). Proof is furnished in the same article, p. 1240, for the assumption of a great complexity of kerosene bases.

nitric acid of sp. gr. 1.260, at a temperature of 170°, was found to give the most promising results, although the yields of reaction products are very poor.

In order to discuss more clearly the important conclusions arrived at from the data obtained in the nitric acid reactions, there are subjoined structural formulas tentatively assigned to four nitric acid reaction products and preceding these the structural formula proposed for the $C_{16}H_{25}N$ base



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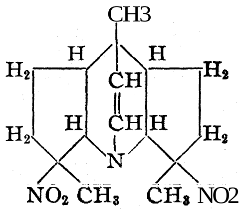

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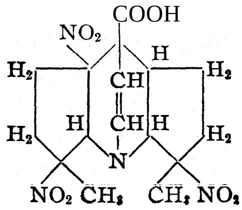

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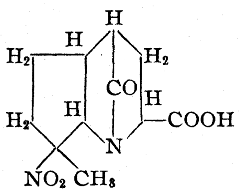

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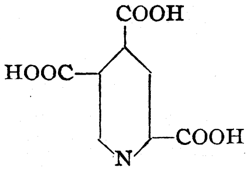
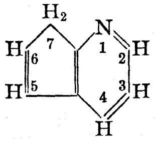
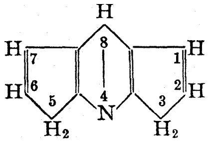


V

The following formulas, VI, C_8H_7N, and VII, $C_{11}H_9N$, for which the names, *pyrindine*[10] and *pyrindacine*,[11] respectively, are proposed, contribute to a simplification of the nomenclature of the products discussed



VI



VIII

There are derived from these parent compounds the names: (I) decahydro-3,5,8-trimethyl-4,8-ethenopyrindacine, (II) decahydro-3,5,8-trimethyl-3,5-dinitro-4,8-ethenopyrindacine, (III) decahydro-3,5-dimethyl-

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[10] Dr. Patterson favors the spelling **pyrindine** rather than pyrindene [*cf.* Zincke, Ann., 290, **321** (1896)] because the compound is a base. Several isomeric pyrindines are possible due to the relative positions of the CH_2 and N [*cf.* Meyer and Jacobson, II, (3) 1050], of which VI is "**1,7-pyrindine.**"

[11] The corresponding hydrocarbon, *indacene*, is shown in the form of derivatives [see M. V. Jonescu, Bull. *soc. chim.*, 37, **916 (1925)**; **41, 1096** (1927)], and bears the same relation to *pyrindacine* as anthracene to *acridine*. As in the case of **pyrindines** a number of isomeric pyrindacines are possible.

3,5,7 a-trinitro-4,8-ethenopyrindacine-8-carboxylic acid, (IV) octahydro-7-methyl-7-nitro-1,4-carbonylpyrindine-3-carboxylic acid.

Formula I, which may be considered elucidated in its most important features, *reflects an important structural relationship between this hydroaromatic base and the petroleum naphthenes.* In view of the wealth of bases in petroleum distillates it is highly probable that the $C_{16}H_{25}N$ product is the forerunner of a family of compounds of a type that may be termed appropriately "Naphthenic Bases," a study of which may contribute to a solution of the difficult structural problems presented by the naphthenic acids.[12]

It soon became evident in this investigation that the $C_{16}H_{25}N$ base represents an unusual type of compound. The failure of all hydrogenation and dehydrogenation experiments to effect a chemical change in the substance makes improbable such products as a heptamethyltetrahydroquinoline or a trimethyldecahydroacridine. Further evidence of the improbability of such structural types is also furnished by the great stability of the base toward alkaline permanganate.

Since in numerous instances it has been established conclusively that the so-called naphthenes are alkylated cyclopentanes, and since the chemical behavior of the $C_{16}H_{25}N$ compound, where its basic properties are not involved, strongly parallels that of methylcyclopentane,[13] a structural interpretation is presented in I that assumes a condensation of two cyclopentane nuclei with a piperidine nucleus. In each of the five-membered rings a tertiary carbon appears in explanation of the fact that, analogous to corresponding napthenes containing one tertiary carbon and forming *mononitro* derivatives,[14] our product yields a colorless, alkali-insoluble, *dinitro* derivative, II. The assumption of a piperidine complex in the molecule is warranted by the formation of product V, $C_8H_5O_6N$, in the nitric acid oxidation. The only structure admissible for this substance is that of a pyridine tricarboxylic acid. All six isomers are known and the properties of our product prove it to be pyridine-2,4,5-tricarboxylic acid, *i. e.*, berberonic acid.[15,16] This substance is of very little importance in proof of structure other than to indicate that the nitrogen in the $C_{16}H_{25}N$

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[12] On the cyclopentane structure of naphthenic acids see Zelinsky, *Ber.*, 57, 51, 57 (1924); Bushong and Humphry, "Eighth International Congress of Applied Chemistry," Vol. VI, p. 58; von Braun, *Z. angew. Chem.*, 43, 1051 (1930).

[13] Wischin, "Die Naphthene," 1901, p. 20, states: "permanganate in neutral as well as in alkaline solution reacts very slightly on naphthenes; only after prolonged action at 40° can a weak oxidizing effect be observed." The extraordinary stability of methylcyclopentane against dehydrogenation was established by Zelinsky, *Ber.*, 45, 678 (1912).

[14] Markownikoff and Konovalow, *ibid.*, 28, 1234 (1895); Kijner, *J. prakt. Chem.*, 56,364 (1897); Markownikoff, *Ann.*, 307,335 (1899).

[15] H. Weidel, *Ber.*, 12, 410 (1879).

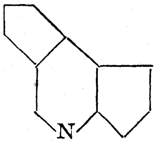
[16] Mumm and Hüneke, *ibid.*, 51, 162 (1918).

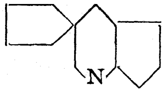
base is in a six-membered ring. It cannot be employed in proof of how the methyl cyclopentane rings are condensed with the six-membered ring, because the higher pyridine-polycarboxylic acids readily split out carbon dioxide at temperatures lower than that at which this pyridine acid was formed. The location of a methyl at the y-position in the piperidine ring harmonizes with our failure to isolate a *trimethyl-trinitro* derivative among the nitric acid reaction products corresponding to the *dinitro* compound, II.

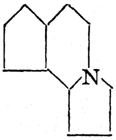
The only unsaturated group assumed in the structurally symmetrical formula assigned the naphthenic base is the etheno bridging between the nitrogen and the y-carbon in the piperidine ring. The fact that this part of the molecule is attacked readily by neither oxidizing nor reducing agents may be plausibly accounted for by steric hindrance. Not until one of the cyclopentane nuclei is disrupted, does the —CH═CH— grouping disappear, as in the $C_{11}H_{14}O_5N_2$ oxidation product, IV, where there is assumed a carbonyl bridging, due to an inner amide formation between a y-carboxyl and the imino group of the piperidine complex. Failure to obtain a nitroso derivative eliminates the isomeric anhydride that would result from dehydration between two carboxyl groups.

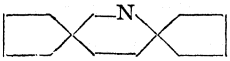
Intermediary between products II and IV is the trinitrocarboxylic acid, III, where the presence of three *tertiary* nitro groups was confirmed by titration; this revealed a monobasic acid, whereas, if there were present in addition to the carboxyl a *secondary* nitro group, the substance would be a dibasic acid.

Despite the satisfactory interpretation of the reactions of the $C_{16}H_{25}N$ base furnished by the structure assigned, there are a number of trinuclear cyclic arrangements other than that proposed in I which remain to be eliminated. As examples of other possible condensations of one six- and two five-membered rings there may be considered







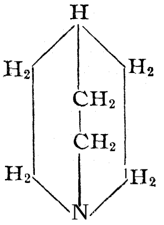


It is obvious that, in the absence of a synthesis of the naphthenic base, absolute proof of structure here presents a very difficult problem in orientation.

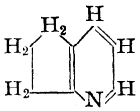
Even granted that the position of contact of the two methylcyclopentane rings with the piperidine ring is as shown in Formula I, the location of methyls at positions 3 and 5, respectively, involves an arbitrary assumption.

From the above discussion it is obvious, and likewise not surprising, that the experimental evidence so far obtained does not offer conclusive proof of the structure of the naphthenic base; still the formulas, tentatively assigned to the different products concerned, should contribute to a clearer conception of their interrelationship.

It is interesting to note that the structure assigned the $C_{16}H_{25}N$ base is related to quinuclidine, i. *e.*, 1,4-ethanopiperidine, A, assumed by Koenigs[17] as one of the parent cyclic nuclei in quinine. Quinuclidine,[18] as well as its alkyl derivatives, is readily synthesized and, like our $C_{16}H_{25}N$ base, piperidine derivatives of this type possess an unusual stability.



Quite recently there has been isolated from Fushun shale oil a base of the formula, C_8H_9N,[19] that is undoubtedly 5,6-dihydropyrindine, B.[19a] This formula not only harmonizes with the pyrindacine structure assigned the $C_{16}H_{25}N$ base but makes it highly probable, even if 5,6-dihydropyrindine itself is not present among the numerous kerosene bases, that compounds of the pyrindine type occur here.



Experimental Part

The Naphthenic Ease, **$C_{16}H_{25}N$**.—After several crystallizations of the picrate from 95% alcohol, the salt is decomposed with ammonium hydroxide, ammonium picrate washed out of the supernatant oil with water and the base dried at 100° in a current of air. In final purification it can be distilled undecomposed at 10–15 mm. pressure.

The following physical constants were determined: b. p. at 746 mm. 278.2"; d_4^{20} 0.9391; n_D^{20} 1.5129. It is a colorless, odorless, optically inactive oil, only slightly soluble in water and readily soluble in the common organic solvents. With the common alkaloidal reagents it forms difficultly soluble salts.

Anal. Calcd. for $C_{16}H_{25}N$: C, 83.12; H, 10.82; N, 6.06. Found: C, 83.25, 83.30; H, 10.78, 10.81; N, 5.95, 6.12. *Mol. wt.* Subs., 0.1694 g.; benzene, 21.915 g.; *At*, 0.183°. Calcd. for $C_{16}H_{25}N$: mol. wt., 231. Found: mol. wt., 211.

Salts of the Naphthenic Base

Picrate.—This salt separates from a hot, alcoholic solution of the base and picric acid in slender, yellow prisms melting at 151°. It is readily soluble in hot alcohol, glacial acetic acid, benzene, acetone and ethyl acetate and only slightly soluble in water, ether and petroleum ether.

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[17] Koenigs, *Ber.*, 37, 3244 (1904).

[18] Löffler and Stietzel, *ibid.*, 42, 124 (1909).

[19] Eguchi, *Bull. Chem. Soc. Japan*, 3, 239 (1928); *Chem. Zentr.*, **100**, 331 (1929).

[19a] Since this paper was submitted to the Journal, one of the authors, W. C. Thompson, has confirmed the structure of the Eguchi base by its synthesis through condensation of hydroxymethylene-cyclopentanone [Wallach, *Ann.*, 329, 114 (1903)] with cyanoacetamide to 2-hydroxy-3-cyano-5,6-dihydropyrindine [*cf.* Sen-Gupta, *J. Chem. Soc.*, **107**, 1347 (1915)], followed by the series of reactions developed by J. von Braun [*Ann.*, 478, 191 (1930), in the conversion of 2-hydroxy-3-cyano-5,6,7,8-tetrahydroquinoline to 5,6,7,8-tetrahydroquinuline. The results of this investigation will be published in the near future.

Anal. Calcd. for $C_{22}H_{28}O_7N_4$: C, 57.39; H, 6.11; N, 12.17. Found: C, 57.00; H, 6.36; N, 12.46.

Acid Sulfate.—The calculated amount of concentrated sulfuric acid is added to the base in glacial acetic acid and the salt precipitated with ether. It crystallizes from acetone in square, colorless plates melting at 196' and is readily soluble in water and alcohol.

Anal. Calcd. for $C_{16}H_{25}N \cdot H_2SO_4$: S, 9.72. Found: S, 9.69.

Hydrochloride.—A hydrochloric acid solution of the base is evaporated to dryness, the residue dissolved in hot acetone and the salt precipitated with ether. It is readily soluble in water and alcohol and crystallizes from acetone in prisms melting at 251°.

Anal. Calcd. for $C_{16}H_{25}N \cdot HCl$: N, 5.23. Found: N, 5.14, 5.38.

Nitrate.—Very characteristic of the base is its behavior toward nitric acid. When it is introduced into an excess of not too dilute nitric acid, two layers are formed. On cooling and vigorous stirring of the upper layer, the nitrate separates with one molecule of water in crystals of octahedral appearance. A convenient method of preparation is to suspend the base in twice its weight of water, add the calculated amount of nitric acid of sp. gr. 1.30. heat until all the oil has disappeared and chill with stirring. It melts at 79°, at 110° is dehydrated and then has a melting point of 141°. Its solubility in water is 1:20 at 30°. The nitrate is readily soluble in alcohol, glacial acetic acid and acetone. Samples with and without water of crystallization were analyzed.

Anal. Calcd. for $C_{16}H_{25}N \cdot HNO_3 \cdot H_2O$: N, 8.97. Found: N, 8.82. Calcd. for $C_{16}H_{25}N \cdot HNO_3$: N, 9.52. Found: N, 9.57.

The chloroplatinate, prepared in dilute hydrochloric acid and then recrystallized from the same medium, is obtained in slender rods decomposing at 240°.

Anal. Calcd. for $(C_{16}H_{25}N)_2 \cdot H_2PtCl_6$: Pt, 22.35. Found: Pt, 22.29.

The zinc chloride salt, prepared by the addition of a solution of zinc chloride to the base in hydrochloric acid, crystallizes from water in rosets of short, pointed prisms melting at 171'. It is readily soluble in alcohol, hot water and hot glacial acetic acid.

Anal. Calcd. for $C_{16}H_{25}N \cdot ZnCl_2$: N, 3.81. Found: N, 4.12.

The mercuric chloride salt, prepared similarly to the zinc chloride salt, is obtained as an oil which on stirring solidifies. It crystallizes from alcohol in clusters of slender rods melting at 157.5'. It is very difficultly soluble in water and quite soluble in hot alcohol and hot glacial acetic acid.

Anal. Calcd. for $C_{16}H_{25}N \cdot HgCl_2$: N, 2.78. Found: N, 2.86.

The methiodide, prepared in quantitative yield by heating the base with an excess of methyl iodide at 100° in a sealed tube for twenty-four hours, is obtained in the form of slender, colorless prisms by crystallization from alcohol, then from water. It begins to soften around 250" and finally decomposes without melting.

Anal. Calcd. for $C_{17}H_{28}NI$: N, 3.75. Found: N, 3.99.

Proof of the Absence of an N-Alkyl Group in the Naphthenic Base.—In accordance with the procedure of Herzig and Meyer,[20] 1 g. of base, 5 g. of ammonium iodide and 12 cc. of hydriodic acid, sp. gr. 1.70, were heated slowly in a current of carbon dioxide up to 300° and this temperature was maintained for two hours longer. No alkyl iodide was formed and the unchanged base after recovery in the usual way was identified by conversion to the picrate. The hydrochloride of the base heated in a current of hydrogen chloride, in accordance with the method of Ladenburg,[21] also gave a negative result

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[20] Herzig and Meyer, *Monatsh.*, 15, 613 (1894).

[21] See Cohen, "Organic Chemistry for Advanced Students," Vol. III, p. 353.

Finally the base was heated with benzoic acid at 250–280° for twelve hours,[22] in the hope of obtaining the benzoyl derivative of a secondary amine and the alcohol corresponding to the alkyl that might be joined to nitrogen. Here again only unchanged base was recovered.

Dehydrogenation Experiments.—One-half gram of base, 2.5 g. of mercuric acetate and 2.5 cc. of 50% acetic acid were heated in a sealed tube at 150° for twelve hours.[23]

There was no separation of mercury and the original base was recovered in the usual way. The method of Kann and Tafel,[24] where distillation with admixed silver sulfate and kieselguhr is employed, gave back the base unchanged. The dehydrogenation method of Borsche,[25] employing pumice stone impregnated with lead dioxide, also failed to alter the base. Finally it was found that the base mixed with zinc dust could be distilled out unchanged.[26]

Action of Bromine on the $C_{16}H_{25}N$ Base.—With an excess of bromine in chloroform solution 1,2,3,4-tetrahydroquinoline is readily converted to tribromoquinoline.[27] When to the naphthenic base in chloroform an excess of bromine is added, there remains after evaporation of the solvent a red, oily residue. This represents a loose bromine addition product, since from its alcoholic solution the characteristic picrate of the original base separates on addition of picric acid. On treatment of the base with bromine water the color of the solution disappears and there is formed a viscous, red-brown gum, insoluble in water and dilute acids and soluble in glacial acetic acid. Caustic soda reconverts this product to the original base.

Since the aromatic base, 2,3,8-trimethylquinoline, accompanies the hydroaromatic base in the 276° fraction of the kerosene bases, their difference in behavior toward bromine is of especial interest. The addition of bromine to a chloroform solution of the aromatic base is followed by an immediate separation of a reaction product crystallizing in light yellow needles. This, however, is a loose bromine addition product since caustic soda solution removes the bromine and restores the original base.

Oxidation with Permanganate.—The naphthenic base in permanganate solution was boiled over a period of one hundred and fifty hours, when the greater part of the base was ethered out unchanged. The remaining solution was then decolorized with sulfur dioxide, filtered, acidified with nitric acid, and, in order to remove free nitric acid, evaporated to dryness. The residue dissolved in water gave with a silver nitrate solution a precipitate that proved to be silver oxalate.

Hydrogenation Experiments.—With sodium and absolute alcohol pyridine is reduced to piperidine,[28] and 5,6,7,8-tetrahydroquinolines to decahydroquinolines.[29] This procedure proved ineffective with the naphthenic base, as did the employment of sodium and amyl alcohol. Without avail reduction with tin and hydrochloric acid was attempted in accordance with the method employed in the conversion of 5,6,8-trimethylquinoline to the corresponding Py-tetrahydroquinoline.[30] Although 1,2,3,4-tetrahydroquinoline is reduced to decahydroquinoline with hydriodic acid and red phosphorus,[31] this form of reduction gave with the naphthenic base likewise a negative result.

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[22] *Cf.* von Braun and Weissbach, *Ber.*, **63**, 489 (1930).

[23] *Cf.* Tafel, *ibid.*, **25**, 1619 (1892).

[24] Kann and Tafel, *ibid.*, **27**, 826 (1894).

[25] Borsche, *Ann.*, **359**, 49 (1908).

[26] *Cf.* Ferratini, *Ber.*, **26**, 1812 (1893).

[27] Hoffmann, Leo and Koenigs, ibid., **16**, 727 (1883).

[28] Ladenburg, *Ann.*, **247**, 43 (1888).

[29] von Braun, Petzold and Seeman, *Ber.*, **55**, 3782 (1922).

[30] Wikander, *ibid.*, **33**, 646 (1900).

[31] Bamberger and Williamson, *ibid.*, 27, 1485 (1894).

Action of Nitric Acid on the Naphthenic Base.—One gram of base is heated in a sealed tube with 10 cc. of nitric acid, sp. gr. 1.260, slowly over a two hour period up to 170° and this temperature then maintained for three hours. The pressure generated makes it inadvisable to employ larger amounts of material. Although the yields were unfavorable, four reaction products in apparently pure form were isolated. These substances of the composition, $C_{16}H_{23}O_4N_3$, $C_{16}H_{20}O_8N_4$, $C_{11}H_{14}O_5N_2$ and $C_8H_5O_6N$, are referred to in the introduction as products, II, III, IV and V, respectively.

For isolation of the nitric acid reaction products, the material from 24 g. of base is combined and concentrated by vacuum distillation to a gummy consistency. In order to remove traces of nitric acid, the residue is taken up in water and the distillation repeated. On addition of 150 cc. of water, product III in poor yield remains undissolved as a smear. The decanted solution is made alkaline to methyl orange with *N*/3 barium hydroxide and filtered from the barium salt of product V. On further addition of barium hydroxide to the phenolphthalein end-point, product II separates and is ethered out. With all basic material removed the barium in the form of hydroxide and nitrate is exactly precipitated as sulfate, the barium sulfate filtered off and the solution evaporated to dryness. The residue is next taken up in a little alcohol and ether added as long as it causes precipitation. From the gummy material obtained in this way, and dissolved in a small volume of hot acetone, there separates after several days' standing in the icebox product IV in crystalline form. Methods of isolating the residual products in the acetone solution have not been worked out, and no attempt was made to identify among the oxidation products volatile, fatty acids.

Product II for purification is converted to its picrate and the latter recrystallized from alcohol in diamond-shaped plates melting at 231°. The picrate is then treated with ammonium hydroxide and the liberated base recrystallized from alcohol in the form of colorless, slender rods melting at 116.5° and distilling even at low pressures with partial decomposition. It is readily soluble in organic solvents and insoluble in water.

Anal. Calcd. for $C_{16}H_{23}O_4N_3$: C, 59.81; H, 7.16; N, 13.09. Found: C, 59.89 H, 7.43; N, 12.80. *Mol. wt.* Subs., 10.8 mg.; camphor, 89.7 mg.; *At*, 15. Calcd. for $C_{16}H_{23}O_4N_3$: mol. wt., 321. Found: mol. wt., 320.

Product III on crystallization from alcohol is obtained in the form of yellow, rhombic plates melting with decomposition at 347°. Although insoluble in water it, unlike product I, is alkali soluble.

And. Calcd. for $C_{16}H_{20}O_8N_4$: C, 48.48; H, 5.05; N, 14.14. Found: C, 47.90; H, 4.92; N, 14.47. *Mol. wt.* Subs., 8.8215 mg.; camphor, 92.7 mg.; At, 11. Calcd. for $C_{16}H_{20}O_8N_4$: mol. wt., 396. Found: mol. wt., 348. *Titration.* Subs., 8.882 mg.: 0.89 cc. of 0.0258 *N* NaOH. Calcd. for $C_{16}H_{20}O_8N_4$ as monobasic acid: 0.87 cc.

Product IV on crystallization from alcohol separates in the form of colorless prisms melting with decomposition at 189–190°. It is readily soluble in water or hot alcohol and only slightly soluble in ether. In contrast to the parent naphthenic base, it is readily oxidized with alkaline permanganate. It does not give colorations with either ferrous sulfate or ferric chloride. Attempts to prepare a nitroso derivative were unsuccessful.

Anal. Calcd. for $C_{11}H_{14}O_6N_2$: C, 51.97; H, 5.51; N, 11.02. Found: C, 52.48; H, 5.43; N, 11.03. *Mol. wt.* Subs., 7.618 mg.; camphor, 92.5 mg.; *At*, 14. Calcd. for $C_{11}H_{14}O_5N_2$: mol. wt., 254. Found: mol. wt., 235. *Titration.* Subs., 0.539 mg.: 3.00 cc. of 0.0257 N NaOH. Calcd. for $C_{11}H_{14}O_5N_2$ as dibasic acid: **2.93** cc.

Berberonic Acid, Product V, crystallizes from water with two molecules of water of crystallization in a network of hair-like needles melting with decomposition at 240–241°. It is readily soluble in cold alcohol and possesses a wide difference in solubility in hot and cold water. With ferrous sulfate it gives even at a dilution of 1 part in 2500 parts of water a blood-red coloration. A characteristic property of this acid is the formation of a calcium salt on boiling its aqueous solution with animal charcoal. This salt crystallizes from water in plates with well-defined, diamond-shaped end faces.

Anal. Calcd. for $C_8H_5O_6N$: C, 45.50; H, 2.37; N, 6.63. Found: C, 45.29; H, 2.56; N, 6.83. *Mol. wt.* Subs., 11.503 mg.; camphor, 118.4 mg.; Δt, 18. Calcd. for $C_8H_5O_6N$: mol. wt., 211. Found: mol. wt., 216. *Titration.* Subs., 16.848 mg.: 9.20 cc. of 0.0257 *N* NaOH. Calcd. for $C_8H_5O_6N$ as tribasic acid: 9.33 cc.

Summary

1. A hydroaromatic base, $C_{16}H_{25}N$, isolated from the crude kerosene distillate as produced at the Oleum Plant of the Union Oil Company of California, is described along with a number of characteristic salts.

2. This base is regarded as 4-methyl-1,4-ethenopiperidine, condensed at 2,3 as well as at 5,6, with methylcyclopentane. In addition to the two cyclopentane nuclei, this structure presents two tetrahydropyridine complexes within the piperidine periphery, so that in all five rings are involved.

3. Corresponding to the structural formula proposed, the $C_{16}H_{25}N$ compound, apart from possessing the properties of a tertiary amine, behaves similarly to methyl cyclopentane.

4. The term "Naphthenic Bases" is proposed for bases like the $C_{16}H_{25}N$ compound of the cyclopentane type, in order to emphasize their relationship to the so-called naphthenes.

5. The claim previously advanced that *"petroleum offers the greatest wealth of nitrogen compounds of any natural source"* is strengthened by the results reported in this paper and the isolation, proof of structure and even synthesis of a host of so-called petroleum bases only await a realization of the attractive field of research presented.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE WEST VIRGINIA UNIVERSITY]

FLUOSILICATES OF ORGANIC BASES. II

BY C. A. JACOBSON[1]

RECEIVED SEPTEMBER 24, 1930 PUBLISHED MARCH 6, 1931

Continuing the work of Jacobson and Pray,[2] eleven new fluosilicates have been prepared and analyzed.

In general, the preparation of these compounds was similar to that recorded in the first paper. The purest Eastman Kodak Co. bases were

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[1] The Author wishes to acknowledge the assistance of the following persons in the completion of the present work: H. McMillen and C. W. Weaver on o-tolidine fluosilicate; E. Stutzman on di-α-, and di-β-naphthylamine fluosilicate; Christine Arnold on di-diphenylamine and m-phenylenediamine fluosilicates; C. G. Rollins on the fluosilicates of ethylaniline, *p*-nitrosodiphenylamine, *p*-aminoazobenzene and *p*-aminobenzoic acid.

[2] Jacobson and Pray, THIS JOURNAL, 50,3055 (1928).

used and always recrystallized if the microscopic examination showed impurities present.

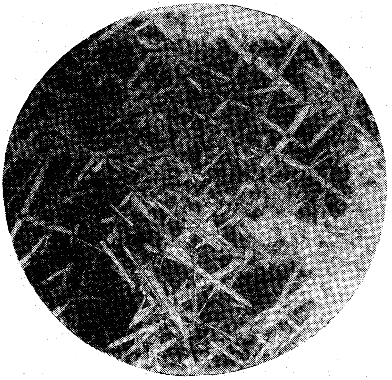

Fig. 1.—*o*-Tolidine fluosilicate.

All the fluosilicates prepared are recorded in the table, giving name, formula, properties and analytical values. They were all recrystallized from 95% ethyl alcohol except Nos. 1 and 9. o-Tolidine fluosilicate was recrystallized from 75% ethyl alcohol and di-nitrosodiphenylamine fluosilicate from a mixture of 95% ethyl alcohol and acetone. The analyses of these compounds indicate that they are all composed of two molecules of the base with one of the acid except Nos. 1, 6 and 7, which have a one to one ratio. This fact is indicated by applying the prefix di- to the name of the compound.

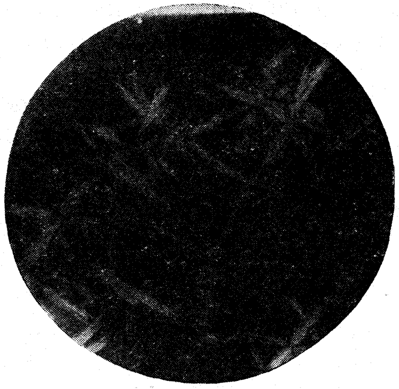

Fig. 2.—Di-a-naphthylamine fluosilicate.

Fig. 3—Di-*β*-naphthylamine fluosilicate.

Table I

Compounds and Data

No.	Fluosilicate of	Formula	Crystal form	M. p., °C.
1	o-Tolidine	$(CH_3NH_2C_6H_3)_2H_2SiF_6$	Tiny microscopic prisms	268–269
2	Di-*α*-naphthylamine	$(C_{10}H_7NH_2)_2H_2SiF_6$	Rosets of needles	218 (dec.)
3	Di-*β*-naphthylamine	$(C_{10}H_7NH_2)_2H_2SiF_6$	Hexagonal plates	236.3
4	Di-m-nitraniline	$(C_6H_4NO_2NH_2)_2H_2SiF_6$	Rhomboidal plates	200
5	Di-diphenylamine	$[(C_6H_5)_2NH]_2H_2SiF_6$	Rods forming rosets	169
6	m-Phenylenediamine	$C_6H_4(NH_2)_2H_2SiF_6$	Long needle-like prisms	243–244
7	*p*-Phenylenediamine	$C_6H_4(NH_2)_2H_2SiF_6$	Six-sided irregular plates	Dec.
8	Di-ethylaniline	$(C_6H_5NHC_2H_5)_2H_2SiF_6$	Pointed prisms	165.3
9	Di-nitrosodiphenylamine	$[(C_6H_5)_2N{=}NO]_2H_2SiF_6$	Butterfly-shaped	124.5 (dec.)
10	Di-*p*-aminoazobenzene	$(NH_2C_6H_4N_2C_6H_5)_2H_2SiF_6$	Long needles	220 (dec.)
11	Di-*p*-aminobenzoic acid	$(NH_2C_6H_4COOH)_2H_2SiF_6$	Long narrow prisms	240–245

In the analyses nitrogen was determined by the **Kjeldahl** method, and the fluosilicic acid radical by the author's own method recorded.[3]

TABLE II

SOLUBILITIES AND ANALYSES

No.	Solubilities in 100 cc. of 95% EtOH at 25°		Nitrogen, % Calcd.	Found			H_2SiF_6, % Calcd.	Found	
1	0.013	0.041 at 35°	9.85	9.17	9.06		40.44	40.52	
2	.1504		6.50	6.36	6.54	6.58	33.48	33.46	33.50
3	.0816	.1248 at 35°	6.50	6.60	6.54		33.48	33.13	33.16
4	.1210	.4736 at 35°	13.34	13.45	13.46		34.29	34.70	34.28
6	2.4492		5.81	6.06	5.84		29.87	29.72	29.74
6	0.005		11.11	11.39	11.26		57.13	57.27	(Av. of 3)
7	.014		11.11	11.89	11.51		57.13	57.43	56.96
8	.979		7.25	7.42	7.43		37.30	37.17	37.41
9	.84		10.37	10.15	10.41		(Colored soln. end-pt. indist.)		
10	.187		15.62	15.73	15.78		(Colored soln. end-pt. indist.)		
11	91		6.94	6.71	6.89		34.45	34.59	34.67

All the above compounds are white in color except No. 6, which is chocolate-brown, No. 7 pinkish, No. 9 indigo and No. 10 cinnamon-brown. They are all stable in the air except No. 4, which turns yellow on long standing, and No. 5, whose surface becomes blue after some weeks exposure to the air.

All are stable in water solution except Nos. 2, 6 and 9. Nos. 3, 4 and 10 also decompose in the presence of water although more slowly. The remaining fluosilicates are all insoluble in water except Nos. 7, 8 and 11, which are readily soluble. No. 3 exhibits a high surface tension and at first floats on the water like lycopodium.

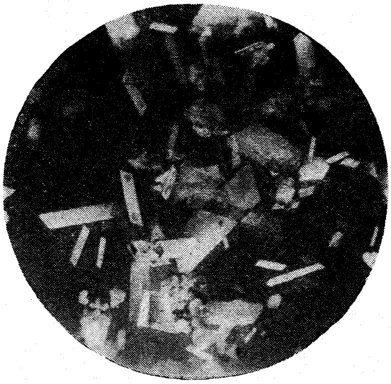

Fig. 4.—Di-m-nitroaniline fluosilicate.

Fig, 5.—Di-diphenylamine fluosilicate.

The fluosilicates are all crystalline compounds possessing definite and characteristic crystal forms, as shown in the accompanying micro photographs. In the case of No. 9, very fine hair-like crystals were obtained from 95% ethyl alcohol, while differently shaped crystals, as shown in

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[3] Jacobson, *J. Phys. Chem.*, 28, 506 (1924).

Fig. 6.—*m*-Phenylenediamine fluosilicate.

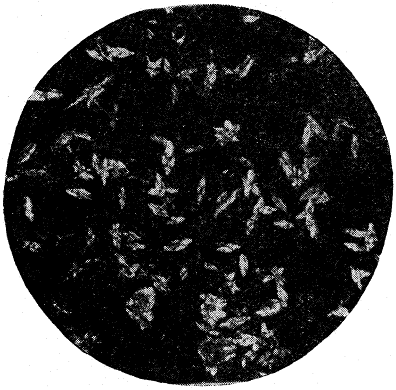

Fig. 7.—*p*-Phenylenediamine fluosilicate.

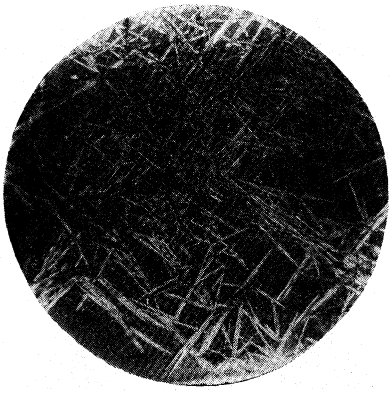

Fig 8.—Diethylaniline fluosilicate.

Fig. 9.—Di-nitrosodiphenylamine fluosilicate.

Fig. 10.—Di-*p*-aminoazobenzene fluosilicate.

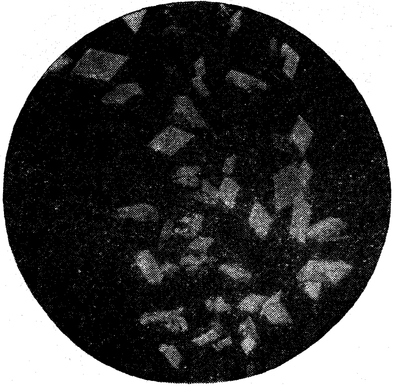

Fig. 11.—Di-*p*-aminobenzoic acid fluosilicate.

the cut, resulted when crystallized from a mixture of ethyl alcohol and acetone.

Fruitless attempts were made to prepare fluosilicates of the following substances: (1) triphenylamine, (2) o-nitroaniline, (3) *p*-nitroaniline, (4) succinimide, (5) dimethyl-a-naphthylamine, (6) benzamide, (7) dimethyl-*p*-toluidine.

Benzidine fluosilicate has been prepared but will be described later.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

LOCAL ANESTHETICS IN THE PYRROLE SERIES. II[1]

BY F. F. BLICKE AND E. S. BLAKE

RECEIVED OCTOBER 2, 1930 PUBLISHED MARCH 6, 1931

The structure of novocaine has been modified by a number of investigators in the hope that a better medicament might be obtained and also in order that more information might be acquired regarding the relationship between structure and local anesthetic action.[2] This has been accomplished by a variation in one or more of the three units A, B and C in the novocaine molecule (I).

$$(4)\ \underbrace{H_2N—C_6H_4—}_{A}CO—O—\underbrace{CH_2—CH_2—N(C_2H_5)_2}_{B\qquad\qquad C}$$

I

The primary object of our investigation was to determine, with regard to local anesthetic activity, the effect of a replacement of 4-aminobenzoyl by 2-pyrroyl and the result of a substitution of 1-pyrryl and 1-pyrrolidyl for the diethylamino group.[3] Thus in the analogs of novocaine which we obtained unit A is represented by benzoyl, 4-aminobenzoyl and 2-pyrroyl,

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[1] This paper represents the second part of a dissertation submitted to the Graduate School by E. S. Blake in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan. The first part of the dissertation was published in THIS JOURNAL, 52, 235 (1930).

This investigation was made possible by the grant of a fellowship by Frederick Stearns and Company and we wish to express our appreciation for the aid which has been given us.

[2] Fränkel, "Die Arzneimittel-synthese," J. Springer, Berlin, 1927, p. 386–395; v. Braun and co-workers, *Ber.*, 52, 2011 (1919); *ibid.*, 55, 1666 (1922); McElvain and co-workers, THIS JOURNAL, 48, 2179, 2239 (1926); *ibid.*, 49, 2835 (1927); 51, 887, 922 (1929); Barnes and Adams, *ibid.*, 49, 1307 (1927); Marvel and co-workers, *ibid.*, 50, 563 (1928); 51, 915 (1929); Tréfuel, Tréfuel and Barbelet, *Bull. sci. pharmacol.*, 37, 184, 240 (1930); *Chem. Abstracts*, 24, 3502 (1930).

[3] Luft [*Ber.*, 38, 4044 (1905)] has described the preparation of 4-(N-piperidyl)-antipyrine, while v. Braun and Lemke [*ibid.*, 55, 3540, 3557 (1922)] prepared 4-(N-pyrrolidyl)- and 4-(N,Δ^3-pyrrolyl)-antipyrine. According to the latter investigators the pyrrolidyl is a stronger antipyretic than the piperidyl or the pyrrolyl derivative.

unit C by 1-pyrryl and 1-pyrrolidyl, respectively, and in some instances the trimethylene group has been substituted for B.

I	$C_6H_5COOCH_2CH_2NC_4H_4$	V	$C_6H_5COOCH_2CH_2CH_2NC_4H_4$
II	$H_2NC_6H_4COOCH_2CH_2NC_4H_4$	VI	$H_2NC_6H_4COOCH_2CH_2CH_2NC_4H_4$
III	$C_4H_4NCOOCH_2CH_2NC_4H_4$	VII	$C_4H_4NCOOCH_2CH_2CH_2NC_4H_4$
IV	$H_2NC_6H_4COOCH_2CH_2NC_4H_8$	VIII	$H_2NC_6H_4COOCH_2CH_2CH_2NC_4H_8$

The benzoyl (I), 4-aminobenzoyl (II) and the 2-pyrroyl (III) derivatives of β-(1-pyrryl)-ethyl alcohol, $C_4H_4NCH_2CH_2OH$, were prepared in the following manner. Potassium pyrrole was condensed with β-chloroethyl acetate with the formation of the acetyl derivative of β-(1-pyrryl)-ethyl alcohol. The latter was hydrolyzed, the alcohol converted into its potassium derivative and then allowed to react with benzoyl chloride. The 4-nitrobenzoyl and the 2-pyrroyl compounds were obtained by a similar series of reactions. Upon catalytic reduction of the 4-nitrobenzoic acid ester, $NO_2C_6H_4COOCH_2CH_2NC_4H_4$, the corresponding 4-amino derivative was formed.

4-Aminobenzoic acid was condensed with ethylene chlorohydrin with the formation of β-chloroethyl 4-aminobenzoate, $H_2NC_6H_4COOCH_2CH_2Cl$. The latter, when heated with pyrrolidine, yielded the 4-aminobenzoyl derivative of β-(1-pyrrolidyl)-ethyl alcohol (IV).

γ-(1-Pyrryl)-propyl alcohol was prepared in a manner similar to that described in the case of pyrrylethyl alcohol and the benzoyl (V), 4-aminobenzoyl (VI) and 2-pyrroyl (VII) derivatives were obtained by methods analogous to those outlined above.

γ-Chloropropyl 4-aminobenzoate, synthesized from 4-aminobenzoic acid and trimethylene chlorohydrin, was condensed with pyrrolidine to form the 4-aminobenzoyl derivative of γ-(1-pyrrolidyl)-propyl alcohol (VIII).

Stovaine (IX) is obtained by benzoylation of methylethyldimethylaminomethylcarbinol. Pyrroylation of this carbinol yielded compound XI. In order to determine the effect of the substitution of a saturated

IX	$(CH_3)(C_2H_5)[(CH_3)_2NCH_2]COCOC_6H_5$	XII	$(CH_3)(CH_3)(C_4H_4NCH_2)COH$
X	$(CH_3)(C_2H_5)(C_4H_8NCH_2)COCOC_6H_5$	XIII	$(C_2H_5)(C_2H_5)(C_4H_4NCH_2)COH$
XI	$(CH_3)(C_2H_5)[(CH_3)_2NCH_2]COCOC_4H_4N$	XIV	$(C_2H_5)(C_2H_5)(C_4H_4NCH_2CH_2)COH$

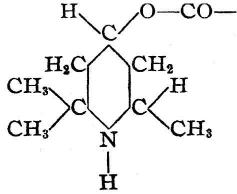
cyclic amine for the dimethylamino group, compound X was prepared by the interaction of methylethylchloromethylcarbinol with pyrrolidine and subsequent benzoylation of the reaction product.

We also synthesized the three tertiary carbinols dimethyl-1-pyrrylmethylcarbinol (XII), diethyl-1-pyrrylmethylcarbinol (XIII) and diethyl β-(1-pyrryl)-ethylcarbinol (XIV). It was hoped that these compounds might be benzoylated and pyrroylated through reaction of the potassium derivatives of the carbinols with benzoyl and pyrroyl chloride, respectively, especially since it was found that stovaine can be obtained from the potassium derivative of methylethyldimethylaminomethylcarbinol and benzoyl chloride. Direct interaction of the carbinols with the acid chlorides yielded only gums or resins since the hydrogen chloride formed during the reaction attacked the pyrrole nucleus. However, the products obtained from the potassium derivatives of the carbinols were oils which we were unable to purify. Although it was realized that the material may have contained a small quantity of unchanged benzoyl chloride, the benzoylation product of carbinol XIII was hydrolyzed and the benzoic acid produced was weighed. The calculated amount of acid was 1.22 g.; the quantity found was 1.18 g. In the event that the compound hydrolyzed was the benzoyl derivative of the carbinol, it seems strange that the material should have been found to be devoid of anesthetic action.

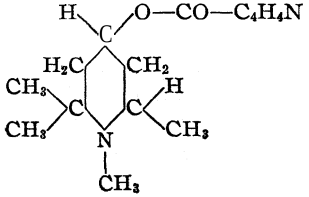
Carbinol XII was obtained by the action of potassium pyrrole on ethyl chloroacetate and subsequent treatment of the ethyl 1-pyrrylacetate with methylmagnesium iodide. When ethylmagnesium bromide was used diethyl-(1-pyrryl)-methylcarbinol (XIII) was formed.

By a similar series of reactions—interaction of potassium pyrrole with ethyl β-bromopropionate and treatment of the ethyl β-(1-pyrryl)-propionate formed with ethylmagnesium bromide—diethyl-(1-pyrryl)-ethylcarbinol (XIV) was synthesized.

In the case of β-eucaine (XV), the benzoyl derivative of the stable form of 2,2,6-trimethyl-4-hydroxypiperidine (vinyldiacetone alkamine), the molecule was modified by the substitution of a 2-pyrroyl for the benzoyl group and the replacement of the 1-hydrogen of the piperidine nucleus by a methyl group (XVI). The latter group was introduced merely in order to facilitate one stage of the synthesis.



XV



XVI

We prepared, in addition, the 4-(2-pyrroyl)-1-methyl derivative of the labile form of 2,2,6-trimethyl-4-hydroxypiperidine. The stable and labile forms of the secondary carbinol were obtained as follows. Diacetone alcohol was converted into mesityl oxide and from the latter diacetoneamine hydrogen oxalate was prepared. Reduction of the oxalate yielded a mixture of the two stereoisomeric forms of vinyldiacetone alkamine. The isomers were separated and methylated. Upon interaction of the potassium derivatives of the alcohols with 2-pyrroyl chloride the desired esters were formed.

In the novocaine series compounds I and V seemed to be inert while the other derivatives produced a distinct local anesthetic effect. The compounds were tested by the application of a concentrated alcoholic solution to the tongue and the inner side of the lips. Because of the burning and drying effect of alcohol on the mucous membrane, it is obvious that the use of this solvent is objectionable. However, in spite of these features of the alcohol the local anesthetic action produced by the compounds tested was unmistakable. The undesirable action of the alcohol is mitigated to a considerable degree by the addition of water but, unfortunately, the products tested although very soluble in alcohol are precipitated upon the addition of any appreciable quantity of water to the alcoholic solution.

Aqueous solutions of the hydrochlorides of compounds IV and VIII produced no anesthetic effect, a behavior which would be expected since novocaine (hydrochloride) is without action on the tongue but novocaine base, in alcohol, exhibits a very decided anesthesia.

-Compounds X and XI, stovaine analogs, were active both as base and hydrochloride, a behavior which is consistent with that of stovaine (hydrochloride) since the latter anesthetizes the tongue.

The base of the 4-(2-pyrroyl)-1-methyl derivative of the stable form of 2,2,6-trimethyl-4-hydroxypiperidine was found to be active; the corresponding derivative of the labile form inactive.

Our investigation has shown that, in certain types of compounds at least, the following substitutions may be made in local anesthetics without loss, in a qualitative sense, of anesthetic activity—the substitution of 2-pyrroyl for benzoyl and 4-aminobenzoyl and the replacement of the dimethyl- and diethylamino by the 1-pyrryl or the 1-pyrrolidyl nucleus.

Experimental Part

β-Chloroethyl Acetate and **γ-Chloropropyl** Acetate.—Four hundred grams of ethylene chlorohydrin was placed in a flask fitted with a reflux condenser and a dropping funnel. The latter contained 450 g. of technical acetyl chloride which was allowed to drop into the chlorohydrin at a very slow rate. During this operation the flask was cooled with ice water and was shaken occasionally. The mixture was then heated for two hours on a steam-bath, cooled and poured into a small quantity of ice water. After the excess acetyl chloride had hydrolyzed, the oil was separated and washed with a concd. solution of sodium bicarbonate until free from hydrochloric acid. The oil was then dried with fused sodium sulfate and distilled through a fractionation column. There was obtained 500 g. of the ester which boiled at 142–145°. The yield was 82% of the calculated amount.

γ-Chloropropyl acetate was prepared from trimethylene chlorohydrin[4] and acetyl chloride in the manner described above. The ester boiled at 168–173°.[5]

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[4] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 112.

[5] Derick and Bissel [This Journal, 38, 2483 (1916)] reported the boiling point to be 160–166°.

β-(1-Pyrryl)-ethyl Alcohol.—Potassium pyrrole was prepared by the addition of 80 g. of potassium to 330 cc. of warm pyrrole in a flask fitted with a reflux condenser. After the potassium had reacted completely, absolute ether was added to the clear solution in order to precipitate the potassium compound in the form of fine crystals, Unless ether is added the potassium pyrrole separates from the cold mixture in the form of a hard cake. The potassium derivative was filtered and washed with absolute ether. The excess pyrrole can be recovered readily from the filtrate by fractionation.

One hundred and fiiteen grams of potassium pyrrole was placed in a flask fitted with a reflux condenser and 100 g. of β-chloroethyl acetate was added in small portions. The mixture was cooled thoroughly during this process. The pasty reaction mixture was heated in an oil-bath to 70° for several hours, then cooled and, after the addition of absolute ether, filtered. Tbe ether was removed from the filtrate on a steam-bath and the residue distilled under diminished pressure. After the material had been fractionated twice there was obtained 28 g. of the acetyl derivative of β-(1-pyrryl)-ethyl alcohol which boiled at 222–225° under 740 mm. pressure. This substance seemed to possess a very slight local anesthetic action. In order to hydrolyze the ester 55 g. of the latter was heated on a steam-bath for several hours with a mixture which consisted of 40 g. of potassium hydroxide, 30 cc. of water and 50 cc. of alcohol. The alcohol and water were removed under diminished pressure and the semi-solid residue was treated with a small quantity of water. The oil which separated was extracted with ether and the ether solution dried with fused sodium sulfate. Upon fractionation 42 g. of B-(1-pyrryl)-ethyl alcohol was obtained which boiled at 110–113° under 12 mm. pressure,

Benzoyl Derivative (I).—Thirteen and two-tenths grams of β-(1-pyrryl)-ethyl alcohol, dissolved in 150 cc. of dry benzene, was heated with 4.8 g. of potassium until all of the metal had disappeared. Sixteen and eight-tenths grams of benzoyl chloride, dissolved in 100 cc. of absolute ether, was then added. A precipitate of potassium chloride formed immediately. After the mixture had been heated at 70° for several hours it was filtered from potassium chloride and the ether and benzene removed under diminished pressure. The residue, after it had been cooled, consisted of crystals contaminated by a small amount of oil. The mixture was placed on a porous plate and after some time the crystalline material was recrystallized from petroleum ether (90–120°). The yield of pure material was 20 g. or 78% of the calculated amount; m. p. 53–55°.

Anal. Calcd. for $C_{13}H_{13}O_2N$: C, 72.52; H, 6.09; N, 6.51. Found: C, 72.36; H, 6.19; N, 6.56.

4-Aminobenzoyl Derivative (II).—We prepared, first, the β-(-pyrryl)-ethyl ester of 4-nitrobenzoic acid in the following manner. Three and three-tenths grams of P-(1-pyrryl)-ethyl alcohol, dissolved in 50 cc. of dry benzene, was heated with 1.2 g. of potassium. After the metal had reacted the mixture was cooled with ice and 5.5 g. of pure 4-nitrobenzoyl chloride,[6] dissolved in 50 cc. of absolute ether, was added in small portions. The reaction mixture became intensely red but the color disappeared after all of the nitrobenzoyl chloride had been added. The mixture was heated to 60° in a bath for one hour and then filtered. The residue was washed with absolute ether and the ether added to the filtrate. After the solvents had been removed under diminished pressure, a dark brown oil was obtained which became solid when it was cooled. The material was pulverized, dissolved in ether and dark colored impurities precipitated by the addition of petroleum ether (20–40°). The solvents were then allowed to evaporate. After recrystallization from alcohol, 5 g. of slightly yellow, crystalline material was obtained which melted at 92–94'.

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[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 75.

In order to obtain the amino compound, 5.2 g. of the nitro derivative, dissolved in 190 cc. of absolute alcohol, was reduced with hydrogen in the presence of 0.3 g. of platinum oxide catalyst[7] under an initial pressure of four atmospheres. The calculated amount of hydrogen was absorbed in twenty-five minutes. After filtration the solvent was removed under diminished pressure and the solid residue recrystallized from a mixture of petroleum ether (90–120") and benzene; m. p. 87–88'.

Anal. Calcd. for $C_{13}H_{14}O_2N_2$: C, 67.78; H, 6.13; N, 12.17. Found: C, 67.71; H, 6.02; N, 12.25.

2-Pyrroyl Derivative (III).—In order to prepare the potassium derivative of **β-(1-pyrryl)-ethyl** alcohol, 6.6 *g.* of the alcohol, 2.4 *g.* of potassium and 100 cc. of dry benzene were heated to 90° in an oil-bath. Seven and seven-tenths grams of **2-pyrroyl** chloride, dissolved in 100 cc. of absolute ether, was added and the mixture heated for several hours. The potassium chloride was removed by filtration and the filtrate heated under diminished pressure in order to remove the solvents. The residue was dissolved in absolute ether and low-boiling petroleum ether added to precipitate dark colored impurities. After evaporation of the solvents the colorless, crystalline material was recrystallized from a mixture of benzene and petroleum ether; m. p. 73–74°.

Anal. Calcd. for $C_{11}H_{12}O_2N_2$: C, 64.67; H, 5.87; N, 13.72. Found: C, 64.72; H, 5.93; N, 13.67.

β-(1-Pyrrolidyl)-ethyl 4-Aminobenzoate (IV).[8]—Five grams of pure **β-chloroethyl** 4-aminobenzoate, which had been prepared from 4-aminobenzoic acid, ethylene **chlorohydrin** and sulfuric acid[9] was heated in a sealed tube with 6 cc. of pyrrolidine for eight hours in a bath at 115–120°. The reaction mixture was treated with water to remove pyrrolidine hydrochloride and excess pyrrolidine and the solid material was dried and recrystallized from a mixture of benzene and petroleum ether; m. p. 98–100°.

Anal. Calcd. for $C_{13}H_{18}O_2N_2$: C, 66.62; H, 7.74; N, 11.98. Found: C, 66.67; H, 7.84; N, 12.09.

γ-(1-Pyrryl)-propyl Alcohol.—This compound was prepared in a manner similar to that described in the case of the ethyl **homolog.** From potassium pyrrole and **γ-chloro**propyl acetate the acetyl derivative of **γ-(1-pyrryl)-propyl** alcohol was obtained. The latter boiled at 127–135° under 13 mm. pressure and 93 g. of the material was obtained from two moles of potassium pyrrole. From 258 g. of the acetate we obtained, by hydrolysis, 150 g. of the pure alcohol. The latter boiled at 229–231° under 743 mm. pressure.

Benzoyl Derivative @).—The material obtained from the interaction of the potassium derivative of the above alcohol and benzoyl chloride boiled at 120–170° under 5 mm. pressure and was evidently a mixture of compounds. One and eighteen-hundredths grams of the oil which boiled at 165–170° under 5 mm. pressure was hydrolyzed with alcoholic potassium hydroxide. There was obtained 0.64 g. of benzoic acid; the calculated amount of acid based on formula V is 0.61 g.

4-Aminobenzoyl Derivative @I).—We prepared first the 4-nitrobenzoyl derivative from 7.5 g. of **γ-(1-pyrryl)-propyl** alcohol, 2.4 g. of potassium and 11.1 g. of 4-nitrobenzoyl chloride. The crude, solid reaction product was dissolved in alcohol and aque-

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[7] "Organic Syntheses," 1928, Vol. VIII, p. 92.

[8] **β-(1-Piperidyl)-ethyl** 4-aminobenzoate has been described by Einhorn and Uhlfelder, *Ann.*, 371, 140 (1909), and **β-(1-piperidyl)-ethyl** benzoate by Laun, *Ber.*, 17, 680 (1884). **β-(1-Pyrrolidyl)-ethyl** benzoate has been obtained by v. Braun, **Braunsdorf** and Rath, *ibid.*, 55,1673 (1922).

[9] German patent 194,748.

ous sodium carbonate was added. The precipitate was removed by filtration, dried and recrystallized from alcohol; m. p. 68–70°. The yield of pure material was 5 g.

Twenty-one and five-tenths grams of the nitro compound, 250 cc. of absolute alcohol and 0.3 g. of platinum oxide catalyst were treated with hydrogen under an initial pressure of four and one-half atmospheres. The reduction required twenty minutes. The catalyst was removed and the amino compound was precipitated in crystalline form by the addition of water. After recrystallization from a mixture of benzene and petroleum ether, the compound melted at 114–116°. The yield was 17 g.; the calculated yield is 19 g.

Anal. Calcd. for $C_{14}H_{16}O_2N_2$: C, 68.81; H, 6.65; N, 11.47. Found: C, 68.74; H, 6.65; N. 11.71.

2-Pyrroyl Derivative (VII).—The potassium derivative of γ-(1-pyrryl)-propyl alcohol, obtained from 6.2 g. of the alcohol, 2 g. of potassium and 75 cc. of dry benzene, was heated for three hours with 6.4 g. of 2-pyrroyl chloride,[10] dissolved in 100 cc. of absolute ether. The potassium chloride was removed by filtration and the solvents distilled under reduced pressure. The residue was dissolved in alcohol and the pyrrole derivative precipitated by the addition of aqueous sodium carbonate. After recrystallization from a mixture of benzene and petroleum ether the product melted at 69–70". The yield was 5 g.

Anal. Calcd. for $C_{12}H_{14}O_2N_2$: C, 66.01; H, 6.46; N, 12.84. Found: C, 66.00; H, 6.48; N, 12.77.

γ-(1-Pyrrolidyl)-propyl 4-Aminobenzoate (VIII).[11]—γ-Chloropropyl 4-aminobenzoate was prepared as follows. Seventy grams of trimethylene chlorohydrin, 103 g. of 4-aminobenzoic acid and 400 g. of sulfuric acid were heated for twelve hours on a steam-bath. The mixture was treated with ice and then with sodium carbonate solution. The crude product was recrystallized from alcohol a number of times and finally from a mixture of benzene and petroleum ether; m. p. 86–87°.

γ-(1-Pyrrolidyl)-propyl 4-aminobenzoate was obtained from γ-chloropropyl 4-aminobenzoate and pyrrolidine in the same manner as compound IV. The compound melted at 84–85° after recrystallization from a mixture of benzene and petroleum ether.

Anal. Calcd. for $C_{14}H_{20}O_2N_2$: C, 67.69; H, 8.12; N, 11.29. Found: C, 67.54; H, 8.20; N, 11.80.

Benzoyl Derivative of Methylethyldimethylaminomethylcarbinol (Stovaine, IX).—Although stovaine is prepared usually by the interaction of the tertiary carbinol and benzoyl chloride[12] we found that it can be obtained in the following manner, a procedure which we used in the case of certain pyrrole derivatives in order to avoid the formation of hydrogen chloride. Three and nine-tenths grams of methylethyldimethylaminomethylcarbinol, dissolved in 50 cc. of dry benzene, was refluxed with 1.2 g. of potassium until the metal had reacted completely. Four and two-tenths grams of benzoyl chloride was then added and the mixture heated to 60–70° for one hour. The potassium chloride was removed by filtration and the filtrate treated with hydrogen chloride. The stovaine hydrochloride, after recrystallization from absolute alcohol, melted at 172–174°. The yield was 5 g.; calcd. yield, 8 g.

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[10] Oddo and Moschini, *Gazz. chim. ital.*, **42**, II, 244 (1912).

[11] Andrews and McElvain [This Journal, 51, 890 (1929)] synthesized γ-(1-pyrrolidyl)-propyl benzoate and γ-(1-piperidyl)-propyl benzoate has been prepared by Dunlop [*J. Chem. Soc.*, 101, 2002 (1912)].

[12] Fourneau, "Organic Medicaments," P. Blakiston's Son and Co., Philadelphia. 1925, p. 218.

Benzoyl Derivative of Methylethyl-(1-pyrrolidyl)-methylcarbinol (X).—Twelve grams of methylethylchloromethylcarbinol[13] and 20 cc. of pyrrolidine were heated in a sealed tube to 115–120° for eight hours. Upon the addition of water to the reaction mixture an oil separated. Since the latter would not solidify when cooled the mixture was made slightly acidic with hydrochloric acid, extracted with ether to remove acid-insoluble material and the aqueous, acid layer was made alkaline with sodium hydroxide. It was then subjected to steam distillation until most of the pprolidine had been removed.[14] The contents of the steam distillation flask were shaken with ether a number of times, the ether layer separated and dried with fused sodium sulfate. After removal of the solvent the tertiary carbinol remained in the form of an oil. The latter was benzoylated in the following manner. Five and seven-tenths grams of the carbinol, 7.1 g. of benzoyl chloride and 25 cc. of dry benzene were heated for three hours on a steam-bath. The mixture was cooled with ice, whereupon the solid, crystalline hydrochloride of the benzoylated carbinol separated. The hydrochloride was found to be very soluble in ethyl acetate and absolute alcohol. The material was recrystallized from the latter solvent but because of the hygroscopic nature of the compound it was converted into the oily base for analysis. The latter was dried for four hours at 65° under 20 mm. pressure.

Anal. Calcd. for $C_{16}H_{23}O_2N$: N, 5.36. Found: N, 5.61.

2-Pyrroyl Derivative of Methylethyldimethylaminomethylcarbinol (XI).—Five and two-tenths grams of methylethyldimethylaminomethylcarbinol[15] was dissolved in 75 cc. of absolute ether. The solution was then added, dropwise, to 5.2 g. of 2-pyrroyl chloride, dissolved in 75 cc. of absolute ether. A black, gummy precipitate formed immediately upon the addition of a small quantity of the carbinol. The solution was decanted from this material and upon the addition of more carbinol a colorless, gummy compound precipitated which after some time became partly crystalline. The material was dissolved in a small amount of hot, absolute alcohol and the solution cooled. The hydrochloride separated in crystalline form upon the addition of absolute ether. After recrystallization from absolute alcohol it melted at 194–195°.

Anal. Calcd. for $C_{12}H_{21}O_2N_2Cl$: N, 10.75; Cl, 13.60. Found: N, 10.83; Cl, 13.55.

Dimethyl-1-pyrrylmethylcarbinol (XI).—Ethyl chloroacetate was prepared from chloroacetyl chloride and absolute alcohol. One mole of potassium pyrrole was covered with absolute ether and heated with 100 g. of ethyl chloroacetate for one hour on a steam-bath. The potassium chloride was removed and the crude ethyl 1-pyrrylacetate, $C_4H_4NCH_2COOC_2H_5$, distilled. It boiled at 110–115° under 16 mm. pressure. The yield was 26 g.

A portion of the ester was warmed for several hours with aqueous sodium hydroxide. The clear, alkaline solution was boiled with charcoal, filtered, the filtrate acidified and then extracted with ether. After evaporation of the solvent the crystalline 1-pyrrylacetic acid was recrystallized from a mixture of benzene and low boiling petroleum ether; m. p. 94–95°.

Methylmagnesium iodide was prepared from 56.4 g. of methyl iodide, 9.6 g. of magnesium and 100 cc. of ether. Twenty-three grams of the above ester was added, drop by drop, to the Grignard reagent and the mixture heated for one hour on a steam-bath. The reaction mixture was decomposed with ice and ammonium chloride and the tertiary carbinol purified by distillation; b. p. 86–88" under 2–3 mm. pressure. The yield was 18 g.

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[13] Ref. 12, p. 214.

[14] After most of the pyrrolidine had distilled a colorless oil began to collect in the receiver. We did not determine whether this oil was the tertiary carbinol or some by-product of the reaction.

[15] Ref. 12. p. 215.

The carbinol was converted into its potassium derivative in the presence of benzene and then treated with the calculated amount of benzoyl chloride and 2-pyrroyl chloride, respectively. The products in both instances were oils.

Diethyl-1-pyrrylmethylcarbinol (XIII).—Forty-five grams of ethyl 1-pyrrylacetate was added to the Grignard reagent obtained from one mole of magnesium and one mole of ethyl bromide. After the mixture had been heated for several hours on a steam-bath, it was decomposed in the usual manner. The tertiary carbinol was purified by distillation; b. p. 108–110° under approximately 1 mm. pressure (bath temperature 125–130°). The yield was 38 g.

Anal. Calcd. for $C_{10}H_{17}ON$: N, 8.37. Found: N, 8 28.

In the case of this carbinol, as well as the following one, the material obtained from the interaction of the potassium derivative and benzoyl chloride was a liquid.

Diethyl-1-pyrrylethylcarbinol (XIV).—One hundred and eighty-one grams of ethyl β-bromopropionate[16] was added, drop by drop, to 126 g. of potassium pyrrole which was cooled with ice. After all of the ester had been added the mixture was heated to 140° for one hour. The potassium chloride was removed and the ethyl β-(1-pyrryl)-propionate distilled; b. p. 119–122" under 14 mm. pressure. The yield was 31 g.

A portion of the ester was hydrolyzed with aqueous sodium hydroxide. The alkaline solution was then boiled with charcoal, filtered and the filtrate concentrated. When the alkaline solution was acidified and cooled the β-(1-pyrryl)-propionic acid precipitated in the form of colorless crystals. The compound is very soluble in hot water. After recrystallization from a mixture of benzene and low-boiling petroleum ether the acid melted at 62–64'. The compound possesses a repulsive odor somewhat similar to that of butyric acid.

The tertiary carbinol was prepared from ethyl β-(1-pyrryl)-propionate and ethylmagnesium bromide. It boiled at 125–128° under 4–5 mm. pressure (bath temperature 135–140°).

Anal. Calcd. for $C_{11}H_{19}ON$: N, 7.73. Found: N, 7.88.

4-(2-Pyrroyl)1-Methyl Derivative of the Stable and Labile Form of 2,2,6-Trimethyl-4-hydroxypiperidine (XVI).—In order to obtain these compounds it was necessary to prepare first vinyldiacetone alkamine. The latter was separated into the stable and labile modifications and these were then pyrroylated in the form of their 1-methyl derivatives.

Diacetone alcohol[17] was converted into mesityl oxide[18] and from the latter diacetoneamine hydrogen oxalate[19] was prepared. We found it unnecessary to convert the oxalate into the free amine[20] in order to reduce it to vinyldiacetone alkamine,[21] since the salt reduces in a satisfactory manner. From 50 g. of the hydrogen oxalate there was obtained 30 g. of the alkamine after the latter had been recrystallized from benzene. The separation of the alkamine into its two isomeric forms was effected by the method of Harries[22] and the latter were then methylated according to the directions given by this investigator.[23]

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[16] Ref. 6, p. 51.

[17] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 45.

[18] Ref. 17, p. 53.

[19] "Organic Syntheses," Vol. VI, p. 28.

[20] E. Fischer, Ber., 17, 1793 (1884).

[21] E. Fischer, *ibid.*, 17, 1794 (1884).

[22] Harries, *Ann.*, 294, 372 (1897).

[23] Harries, *ibid.*, 417, 178 (1918). Conversion of the mixture of the two stereoisomers into the labile form of the alkamine by means of sodium amylate in amyl alcohol is described on p. 274 of this reference. However, the amount of amyl alcohol (40 cc) employed by Harries seems too small and we were obliged to use 100 cc. of the solvent.

The potassium derivative of the stable form of 1-methylvinyldiacetone alkamine was prepared in the following manner. Seven and eighty-five hundredths grams of the stable 1-methyl alkamine, dissolved in 50 cc. of dry xylene, was treated with 1.95 g. of potassium and the mixture refluxed for five hours. The mass should be stirred during this time to prevent the formation of a hard cake. Seven and seventy-four hundredths grams of 2-pyrroyl chloride, dissolved in 125 cc. of absolute ether, was added dropwise to the hot suspension of the potassium derivative. During this process the mixture was shaken constantly. The material was heated for ten minutes, cooled, filtered, the filtrate cooled with ice and treated with hydrogen chloride. The precipitated hydrochloride was found to be very hygroscopic, at least in the crude state. It was separated, dissolved in water and the compound precipitated as the base by the addition of ammonium hydroxide. The oily base was extracted with ether, the ether solution dried with fused sodium sulfate and the solvent removed. When the oily residue was cooled with ice and rubbed under low-boiling petroleum ether it became solid. The yield of crude product was 9 g. After recrystallization from petroleum ether the compound melted at 106–107°.

Anal. Calcd. for $C_{14}H_{22}O_2N_2$: C, 67.14; H, 8.86. Pound: C, 67.14; H, 8.87.

When the base was dissolved in absolute ether and a saturated ether solution of picric acid added a yellow picrate precipitated. After recrystallization from dilute alcohol the latter melted at 192–193°.

Seven and eighty-five hundredths grams of the labile form of 1-methylvinyldiacetone alkamine was converted into the potassium derivative and pyrroylated in the manner described above. There was obtained 7 g. of the crude pyrroyl derivative. After recrystallization from petroleum ether it melted at 106–107°. Since this melting point was identical with that found in the case of the pyrroyl derivative of the stable form of 1-methylvinyldiacetone alkamine, a mixed melting point of the two compounds was determined; this was found to be 80–83°.

Anal. Calcd. for $C_{14}H_{22}O_2N_2$: C, 67.14; H, 8.86. Found: C, 67.19; H, 8.89.

Notes on the Preparation of Pyrrolidine.—This compound was prepared from adipic acid[24] according to a series of reactions described by Miiller and Sauerwald[25] and by v. Braun and Lemke.[24] The methods described below were found by us to be satisfactory for the preparation of certain intermediates. Adipamide can be obtained conveniently by the following procedure. Adipic acid was treated with the amount of sodium carbonate solution required for the formation of the disodium salt and the solution evaporated to dryness. Thirty-seven grams of the oven-dried salt was placed in a round-bottomed flask, fitted with a reflux condenser, mixed thoroughly with 28 g. of pure phosphorus oxychloride and heated for five hours in an oil-bath to 50–55°. Because of the tendency of the mixture to form a hard cake, the yield of acid chloride would, undouhtedly, have been increased if the mixture had been stirred. The acid chloride was not isolated but was converted into the acid amide by the addition of the reaction mixture, in small amounts, to ten times the calculated quantity of a technical grade of ammonia water. The yield of the crude amide, based on adipic acid, was 70% of the calculated amount.

The following method for the preparation of 4-toluenesulfonamide is devoid of danger and more convenient than that described in the literature[26] since the use of a pressure bottle is avoided. Six to ten times the calculated amount of technical ammonium

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[24] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 9; v. Braun and Lemke, *Ber.*, **55**, 3529 (1922).

[25] Miiller and Sauerwald, *Monatsh.*, 48, 157 (1927).

[26] Inglis, *J. Soc. Chem. Ind.*, 37, 289T (1918).

hydroxide was poured into a large beaker, heated almost to the boiling point and stirred vigorously with a mechanical stirrer. 4-Toluenesulfonechloride was then added in small portions. A vigorous reaction ensued with each addition of the chloride. After all of the material had been added the clear solution was cooled, whereupon the amide precipitated. The latter was separated, dissolved in boiling water and treated with charcoal. After filtration the sulfonamide separated from the cold, concentrated solution in the form of colorless crystals.

Summary

Eight analogs of novocaine and several compounds analogous to stovaine and β-eucaine have been prepared and tested for local anesthetic action by application to the tip of the tongue. It was found, at least as far as the compounds discussed in this paper are concerned, that the local anesthetic action of a compound can be retained by the substitution of 2-pyrroyl for the benzoyl and the 4-aminobenzoyl group and by the replacement of dimethyl- and diethylamino by the 1-pyrryl and I-pyrrolidyl nuclei.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

DISTIBYLS. I. TETRAPHENYLDISTIBYL. ATTEMPTS TO OBTAIN TETRAPHENYLDIBISMUTHYL[1]

BY F. F. BLICKE, U. O. OAKDALE AND F. D. SMITH

RECEIVED OCTOBER 2, 1930 PUBLISHED MARCH 6, 1931

We began our present study in the hope that we might obtain tetraphenyldistibyl, $(C_6H_5)_2Sb-Sb(C_6H_5)_2$, and tetraphenyldibismuthyl, $(C_6H_5)_2Bi-Bi(C_6H_5)_2$, compounds analogous to the diarsyls[2] which have been investigated recently in this Laboratory. It was found that the first mentioned compound could be prepared from the interaction of diphenylstibyl iodide and sodium hypophosphite.[3]

Tetraphenyldistibyl, in solution, proved to be extremely reactive toward oxygen and the gas was absorbed with the same rapidity which is so characteristic of a solution of *a* tetra-aryldiarsyl or a triarylmethyl; hence the preparation of the distibyl was carried out in a free radical apparatus and the product isolated in an atmosphere of nitrogen or carbon dioxide.

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[1] This paper represents the first part of a dissertation to be submitted to the Graduate School by U. O. Oakdale in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

This investigation was made possible by the aid of the Parke, Davis and Company Fellowship and by a grant from the Faculty Research Fund of the University of Michigan.

[2] Blicke and Smith, THIS JOURNAL, 51, 2272 (1929); Blicke, Weinkauff and Hargreaves, *ibid.*, 52, 780 (1930); Blicke and Smith, *ibid.*, 52, 2937 (1930).

[3] Schmidt [*Ann.*, 421, 235 (1920)] stated that tetraphenylstibyl oxide, $(C_6H_5)_2Sb-O-Sb(C_6H_5)_2$, when treated with hypophosphorous acid, yields a yellow compound which he thought might be tetraphenyldistibyl. However, no analysis or further description of the material was recorded.

The amount of oxygen absorbed corresponded to that required for the formation of tetraphenylstibyl peroxide, $(C_6H_5)_2Sb-O-O-Sb(C_6H_5)_2$. The colorless, crystalline distibyl possessed a sharp melting point and dissolved in organic solvents with the formation of colorless solutions.

Diphenylbismuthyl iodide, dissolved in bromobenzene, was shaken with molecular silver, mercury, zinc powder and copper bronze, respectively. In the case of the first two metals black precipitates were formed. However, none of the solutions obtained absorbed oxygen. Sodium hypophosphite, at ordinary temperature, did not seem to react with an alcoholic solution of diphenylbismuthyl iodide. When the mixture was warmed a black product was produced. A mixture of diphenylbismuthyl iodide, bromobenzene and copper was placed in an absorption flask, connected with an oxygen reservoir, and shaken vigorously for eight hours. The absorption of oxygen, based on peroxide formation, was approximately 50% of the calculated amount. Similar results were obtained with molecular silver.

Experimental Part

Diphenylstibyl Iodide.—Two hundred grams of crude, dry phenylstibinic acid[4] was dissolved in 500 cc. of hydrochloric acid and 250 cc. of water added to precipitate colored impurities. After filtration the solution of phenylstibinic acid was cooled with ice and treated with sulfur dioxide for three hours. The mixture was then allowed to remain in an ice-bath for six hours. The phenyldichlorostibine,[5] which had separated in crystalline form, was filtered with suction. To prepare phenylstibine oxide a cold acetone solution of phenyldichlorostibine was added, dropwise, to cold dilute ammonia water. The mixture was stirred vigorously during this process and kept cold by the addition of icr The precipitated phenylstibine oxide was filtered with suction, washed with acetone and dried.

Twenty-gram portions of finely powdered, crude phenylstibine oxide were placed in 250-cc. Erlenmeyer flasks fitted with two-holed stoppers through which inlet and outlet tubes were inserted. A stream of dry nitrogen was passed through the flasks and the latter were heated at 90° in an oil-bath for two hours. The viscous reaction products, which contained tetraphenylstibyl oxide, were extracted several times with hot alcohol, the alcoholic extracts filtered and the alcohol removed.[6] The oily residue obtained from each twenty-gram portion of phenylstibine oxide was treated with 10 cc. of acetic acid and stirred, whereupon the material crystallized almost immediately. This substance, diphenylstibyl acetate, was filtered with suction and recrystallized from acetic acid; 1 cc. of acetic acid was used for each gram of the acetate; m. p. 133–135°.[7]

In order to convert the acetate into the corresponding chloride or bromide, or the chloride into the iodide, it is essential that all products should be in a very pure state before the conversion is attempted.

For the preparation of diphenylstibyl chloride 20 g. of pure diphenylstibyl acetate was dissolved in 60 cc. of hot acetic acid. The solution was cooled quickly to room

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[4] Schmidt, *Ann.*, 421, 189 (1920).

[5] Solutions of this material are powerful skin irritants.

[6] This process represents a slight modification of that used by Schmidt [*Ann.*, 421, 234 (1920)] for the conversion of phenylstibine oxide into tetraphenylstibyl oxide.

[7] Schmidt [*Ann.*, 429, 140 (1922)] recorded the melting point as 132°.

temperature and 80 cc. of hydrochloric acid was added immediately in small portions. The mixture was cooled during the addition of the hydrochloric acid. The chloride precipitated at once in crystalline form and was recrystallized from an equal weight of acetic acid; m. p. 68°.[8]

When diphenylstibyl acetate was dissolved in hot acetic acid, the solution cooled to room temperature and an excess of 48% hydrobromic acid added an oil precipitated. When cooled the latter became solid. After three recrystallizations from acetic acid the compound, undoubtedly diphenylstibyl bromide, melted at 86°.

Diphenylstibyl iodide was prepared as follows. Twenty grams of the chloride, dissolved in 25 cc. of pure acetone, was added to three times the calculated amount of sodium iodide dissolved in the same solvent. After twelve hours the sodium chloride was removed and the acetone allowed to evaporate spontaneously. The crystalline iodide, obtained after the addition of water to the residue, was recrystallized twice from acetic acid and twice from absolute alcohol; m. p. 68–70". The iodide is not affected by cold water and is hydrolyzed only very slowly by boiling water.

Anal.[9] Calcd. for $C_{12}H_{10}SbI$: Sb, 30.23; I, 31.51. Found: Sb, 30.20; I, 31.42.

Neither diphenylstibyl iodide nor triphenylmethyl bromide, dissolved in bromobenzene, absorbs oxygen. When diphenylstibyl iodide (0.003 mole) and triphenylmethyl bromide (0.003 mole) were put into a test-tube, the latter constricted and then filled quickly with bromobenzene which had been saturated with nitrogen a deep red solution was formed immediately. When the tube was broken in an oxygen absorption apparatus[10] 51 cc. of oxygen was absorbed very rapidly. This quantity of oxygen is more than that required for the formation of triphenylmethyl peroxide (34.2 cc.) and is less than that necessary for the formation of both triphenylmethyl peroxide and tetraphenylstibyl peroxide. A phenomenon entirely analogous to that described above is observed when diphenylarsyl iodide and triphenylmethyl bromide are mixed.[11]

Action of Metals on Diphenylstibyl Iodide.—Two tubes were prepared each of which contained diphenylstibyl iodide, bromobenzene[12] and copper bronze.[13] After the tubes had been shaken for a definite period of time the one tube was broken in an oxygen absorption apparatus while the contents of the other tube were analyzed for copper halide. Several series of such tubes were shaken for different periods of time. The data obtained showed that the percentage of iodine removed, which should serve as a measure of the amount of tetraphenyldistibyl formed, did not correspond to the percentage of oxygen absorbed. The latter was calculated based on the assumption that tetraphenylstibyl peroxide, $(C_6H_5)_2Sb–O–O–Sb(C_6H_5)_2$, is the primary product of the oxidation. These results indicate that the distibyl undergoes decomposition or that it is rendered inactive toward oxygen by combination with unchanged diphenylstibyl iodide or the copper halide. However, we have shown that the isolated distibyl, dissolved in bromobenzene, retains its activity toward oxygen for a period of several days at least.

In one instance the distibyl was allowed to absorb oxygen as fast as it was formed. One and six-tenths grams of diphenylstibyl iodide, 15 cc. of bromobenzene and 2 g. of copper were placed in an absorption flask attached to a reservoir filled with oxygen and

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[8] Michaelis and Giinther, Ber., 44, 2318 (1911).

[9] Method of Thompson and Oakdale, THIS JOURNAL, **52,** 1195 (1930).

[10] Gomberg and Schoepfle, *ibid.*, **39,** 1661 (1917).

[11] Blicke and Smith, *ibid.*, **51,** 2275 (1929).

[12] This solvent was used because of its comparatively low vapor pressure. Gomberg and Schoepfle, *ibid.*, **39,** 1661 (1917).

[13] Magnesium powder, molecular silver, mercury and zinc dust were tried but only copper and zinc seemed to remove the halogen rapidly.

the absorption flask was shaken vigorously and continuously. After five minutes 20 cc., after one hour 32 cc. and after nine hours 44.8 cc., the amount of the gas calculated for peroxide formation, had been absorbed. An analysis of the copper halide formed showed that practically all of the iodine had been removed from the diphenylstibyl iodide at the end of nine hours.

Tetraphenyldistibyl.—Three and two-tenths grams of diphenylstibyl iodide, dissolved in 25 cc. of absolute alcohol, was poured into a free radical apparatus[14] of 125-cc. capacity. One and three-tenths grams of sodium hypophosphite was dissolved in 5 cc. of water and 20 cc. of alcohol added. This solution was then poured into the radical apparatus. The reaction mixture was protected from light and allowed to remain at ordinary temperature for twelve hours. The distibyl separated from the mixture in the form of pale yellow-green needles. The liquid was decanted through the stopcock with the aid of suction and the product was washed several times with small amounts of alcohol, whereupon it became practically colorless. The compound was dried by allowing the apparatus to remain attached to the suction pump for six hours. The material was then removed from the radical apparatus in the manner described previously in the case of diarsyls.[15] The amount of distibyl isolated was usually somewhat in excess of one gram.

The product when pure was practically colorless and the copper wire test proved it to be halogen free. In a sealed tube filled with nitrogen it melted at 121–122°. In order to prevent oxidation during the weighing of the material it was found advantageous to compress the distibyl in the form of tablets in a tablet machine. Each tablet was then weighed in a closed tube, filled with nitrogen, just large enough to contain it.

Anal.[9] Calcd. for $C_{24}H_{20}Sb_2$: Sb, 43.93. Found: Sb, 44.13.

The diarsyl reacts instantly with iodine. In an apparatus filled with nitrogen there was placed 0.4320 g. of the distibyl. The latter was then dissolved in 15 cc. of benzene and a $N/10$ solution of iodine in carbon tetrachloride was added. The iodine color disappeared instantly but after 15.8 cc. of the solution had been added a permanent color was produced. The calculated amount of iodine solution necessary for the formation of diphenylstibyl iodide is 15.7 cc. The solution was poured into a dish and the carbon tetrachloride evaporated. The yellow, crystalline residue was washed with a very small amount of acetic acid; m. p. 64–65". Mixed with diphenylstibyl iodide it melted at the same temperature.

Potassium permanganate, dissolved in acetone, is decolorized instantly by the distibyl.

A portion of the isolated tetraphenyldistibyl, which weighed 0.7609 g., was dissolved in bromobenzene and the solution preserved in a sealed tube, protected from light for four days. The tube was then broken in an oxygen absorption apparatus. Twenty-nine cc. of oxygen was absorbed almost instantly; the calculated amount is 29.4 cc.

Triphenylbismuthine.—Phenylmagnesium bromide was prepared from 80 g. of bromobenzene (0.5 mole), 12 g. of magnesium and 300 cc. of ether. After the addition of 200 cc. of dry benzene the solution was stirred vigorously and 41 g. of finely-divided, freshly distilled bismuth trichloride (0.13 mole)[16] was added in five portions during the

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[14] Gomberg and Schoepfle, THIS JOURNAL, 39, 1659 (1917). The lower stopcock on the apparatus was removed.

[15] Blicke, Weinkauff and Hargreaves, ibid., 52, 782 (1930).

[16] The best quality of bismuth trichloride which we could obtain contained considerable liquid. The material was drained thoroughly, placed on a porous plate and the latter put into a desiccator. After several days the chloride was distilled from a retort with a very short side arm.

course of one-half hour. The mixture was then heated on a steam-bath and stirred for four hours. The mixture was decomposed with ice and ammonium chloride, the ether layer separated and dried with fused sodium sulfate. After removal of the solvent the oily residue soon solidified. The material war washed with petroleum ether (30–60°); m. p. 76–77°; yield, 48 g., or 84% of the calculated amount.[17]

Diphenylbismuthyl Iodide.—Twenty three grams of diphenylbismuthyl chloride[18] was dissolved in 200 cc. of absolute alcohol, 9 g. of solid sodium iodide added and the mixture shaken for twelve hours. It was then poured into 600 cc. of boiling water. Diphenylbismuthyl iodide separated in the form of yellow flakes. The latter were filtered, washed with water and dried in a vacuum desiccator. The product was treated with hot ethyl acetate in order to dissolve the diphenylbismuthyl iodide, the mixture cooled to room temperature and filtered to remove the red by-product. The solvent was distilled from the filtrate under diminished pressure in a stream of nitrogen. The iodide was powdered, triturated with 20 cc. of petroleum ether (30–60°) in order to remove triphenylbismuthine, the petroleum ether decanted and the process repeated several times; m. p. 132–134°.[19]

Diphenylbismuthyl iodide, dissolved in acetone, instantly decolorizes potassium permanganate dissolved in the same solvent. If a carbon tetrachloride solution of iodine is added to the bismuthyl iodide, dissolved in benzene, the first portion of the iodine solution is decolorized immediately. Upon further addition of iodine a brick-red and then a brown precipitate is formed.

Summary

Tetraphenyldistibyl, $(C_6H_5)_2Sb–Sb(C_6H_5)_2$, has been prepared from diphenylstibyl iodide and sodium hypophosphite. The distibyl, in solution, is just as reactive toward oxygen as solutions of tetra-aryldiarsyls or triarylmethyls.

We have not been able to obtain tetraphenyldibisrnuthyl by the methods used for the preparation of the analogous arsenic and antimony compounds.

Ann Arbor, Michigan

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[17] From phenylmagnesium bromide and bismuth trichloride Pfeiffer [*Ber.*, 37, 4622 (1904)] obtained a 25% yield of triphenylbismuthine.

[18] Challenger and Allpress, *J. Chem. Soc.*, 107, 19 (1915).

[19] Gillmeister [*Ber.*, 30, 2843 (1897)] obtained the iodide from triphenylbismuthine dichloride and sodium iodide.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

OPTICALLY ACTIVE ALPHA-PINENES[1]

BY F. H. THURBER AND R. C. THIELKE

RECEIVED OCTOBER 3, 1930 PUBLISHED MARCH 6, 1931

Since there is some doubt regarding the purity of a-pinenes obtained from natural sources, and likewise regarding the purity of derivatives prepared from them, we have obtained pure products by the method devised by Lynn,[2] that is, by the preparation of the nitroso chlorides of the active pinenes, recrystallization of these compounds to insure their purity and finally decomposition of the nitroso chlorides with dimethylaniline to set free the pinenes. In this preparation we have found that the presence of small amounts of water aided in the formation of the nitroso chloride. In fact, we were able to obtain only traces of the desired product previous to this discovery. Lynn in a private communication informed us that in some runs the nitroso chloride precipitated and in others it did not precipitate. Apparently water catalyzes the reaction. The hydrochlorides of pure dextro, levo and inactive pinenes were prepared and their optical rotations observed. The rotations of the active pinenes were equal and opposite in sign. Methods used in the preparations and results observed are given below in the experimental part.

Preparation of Dextro and Levo α-Pinenes.—Dextro a-pinene was obtained from Port Orford cedar oil by the method previously outlined,[3] that is, by fractionation of the oil and distillation over sodium. Levo or-pinene was obtained from Douglas Fir balsam. The method of purification was identical with that used for the dextro compound. The constants observed for the levo compound were b. p. 155–156°, $[\alpha]_D^{20}$ −42.6". n_D^{20} 0.4676; d_{20} 0.8598. It is of interest to note that there is an almost unlimited supply of Douglas Fir balsam available.

a-Pinene with a low specific rotation was obtained from American turpentine oil. It was used for the preparation of the inactive nitroso chloride by the method outlined by Wallach.[4]

Active Nitroso Chlorides.—These compounds were prepared by the method outlined below. The method is given in some detail since the exact conditions for the preparation of such compounds have not been published up to this time.

To 40 cc. of I-or-pinene, 40 cc. of methyl alcohol (10% water by volume) and 40 cc. of ethyl nitrite were added. The mixture was placed in a wide-mouthed bottle closed with a stopper bearing a thermometer and mechanical stirrer, and was kept at a temperature of −20" during the addition of the theoretical amount of hydrochloric acid. The hydrochloric acid solution was prepared by passing hydrogen chloride gas into 90% methyl alcohol until an approximately 5 *N* solution was obtained. It was found to be advisable to introduce the alcohol–acid solution below the surface of the liquid and to cool the addition tube through which the acid flowed in order to prevent local super-

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[1] From the thesis submitted by R. C. Thielke in partial fulfilment of the requirements for the degree of Master of Science, 1931.

[2] Lynn, THIS JOURNAL, 41, 361 (1919).

[3] Thurber, *Ind. Eng. Chem.*, 19, 739 (1927).

[4] Wallach, *Ann.*, 253, 251 (1889).

heating. A period of approximately two and one-half hours was required for the addition. After all of the acid had been added the reaction mixture was allowed to stand for a short time and was then filtered to remove the inactive derivative which had precipitated.

The filtrate was immediately cooled to −20° and another 200 cc. of cold 90% methyl alcohol added to it. The mixture was then allowed to stand for twenty-four hours, the temperature being maintained at −20° to insure complete precipitation of the active nitroso chloride. Some crystals usually appeared almost immediately after the addition of the cold 90% alcohol. The crystals were removed by filtration and were purified by recrystallization from a 1:2 mixture of chloroform and methyl alcohol.

Dextro pinene nitroso chloride was prepared from d-pinene in a similar manner. However, pinene from Port Orford cedar oil does not yield an inactive nitroso chloride, so that the removal of this product is dispensed with. The yield varied with the type of pinene used but was always very low, usually about 2 g. per run.

Properties of Pinene **Nitroso** Chlorides.—The active nitroso chloride decomposes at room temperature to a brown oily mass in a period of about three weeks. At −20° the compound is stable for a much longer period of time. Some attempts were made to determine the molecular weights, by the freezing point method, of both the active and inactive nitroso chlorides. Definite results could not be obtained but rather high molecular weights were indicated. The active nitroso chlorides are considerably more soluble than the inactive in such solvents as benzene. We expect to make a study of the molecular weights of these compounds at some later time. After recrystallization the following constants were observed.

Nitroso chloride....	dl-	d-	*l*-
M. p., °C..........	115	89.5	90.0
$[\alpha]^{20}_{D}$ (in benzene)..	0.0	+396.2	−366.8

These compounds are somewhat unstable near their melting points and different observers may obtain widely varying melting points, depending upon the rate of rise of temperature of the melting point bath.

Optically Active **Pinene** from **the Nitroso** Chloride Derivative.—The method described by Tilden was used.[5] Twenty grams of a-pinene nitroso chloride was warmed with a mixture of 24 g. of dimethylaniline and 60 cc. of 95% ethyl alcohol. The liberated pinene was recovered by steam distillation and was then washed and purified by refluxing over metallic sodium; yield, 8 *g*. While this is not a large amount of material to work with we were able, by using small-sized apparatus, to determine the physical properties of the pinenes and to prepare their hydrochlorides and determine their properties. The physical properties of the pinenes synthesized are tabulated below.

		B. p., °C. (760 mm.)	$[\alpha]^{20}_{D}$	$[\alpha]^{20}_{D}$ (in alc. soln.)	d_{20}	n^{20}_{D}
Regenerated	dl-a-pinene	155–156	0.00	0.00	0.8592	1.4664
Regenerated	d-a-pinene	155–156	+51.14	$53.91	.8591	1.4663
Regenerated	I-a-pinene	155–156	−51.28	−54.04	.8590	1.4662

A tube 2.95 cm. long and holding 1 cc. of liquid was used for the direct determination of the specific rotation, while a 10-cm. tube was used for the determinations in 4% alcohol solution. Apparently the solvent increased the rotation numerically to a slight degree. The main point, however, is that the rotations are equal and opposite in sign within the limits of experimental error. The samples were considered to be pure and were used for the preparation of the hydrochlorides.

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[5] Tilden, *J. Chem. Soc.*, 85, 759 (1904).

α-Pinene Hydrochloride.—The hydrochloride was prepared by saturating 3-cc. samples of pinene with dry hydrochloric acid gas, at a temperature of from 10–15°. Thereafter the mixture was kept at −5° for one hour. The product was then filtered with suction and recrystallized from five times its weight of absolute methyl alcohol. The alcohol was removed by suction filtration and the melting points and specific rotation were determined immediately. These properties are tabulated below.

	M. p. (corr.), °C.	$[\alpha]_D^{20}$ (1 % alcohol solution)
dl-a-Pinene hydrochloride	132	0.00
d-α-Pinene hydrochloride	132	4–33.52
l-α-Pinene hydrochloride	132	−33.24

The chief point of interest here is that the optical rotations are again equal and opposite in sign within the limits of experimental error. When samples were allowed to stand in the air for even very short periods of time the melting points were somewhat lower. Undoubtedly this accounts for the wide range of melting points (118–133°) reported in the literature.

Summary

1. Samples of pure d-a-pinene, 1-a-pinene and dl-a-pinene were prepared and their physical properties determined. 2. The conditions necessary for the formation of active a-pinene nitroso chloride were worked out. 3. It was found that when methyl alcohol is used as a solvent a small amount of water must be present to bring about the formation of the active nitroso chloride. 4. The hydrochlorides of dextro, dl and levo α-pinene were prepared and their properites studied. 5. Contrary to reports in many texts and journal articles these compounds exhibit a normal behavior, that is, *dl*-α-pinene yields an inactive hydrochloride and the active pinenes yield active hydrochlorides whose rotations are equal and opposite in sign. 6. A study of the molecular weights of the nitroso chlorides will be made later.

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[CONTRIBUTION FROM THE NEWPORT CHEMICAL CORPORATION]

SEVERAL NEW 4'-SULFO-ORTHO-BENZOYLBENZOIC ACID DERIVATIVES AND THE CORRESPONDING ANTHRAQUINONE COMPOUNDS[1]

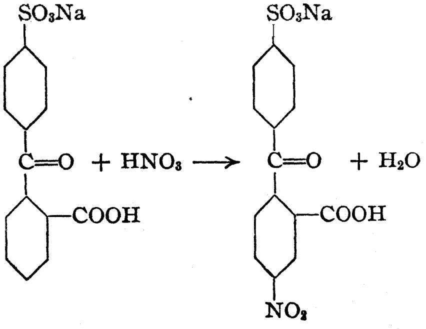
BY IVAN GUBELMANN, H. J. WEILAND AND O. STALLMANN

RECEIVED OCTOBER 30, 1930 PUBLISHED MARCH 0,1931

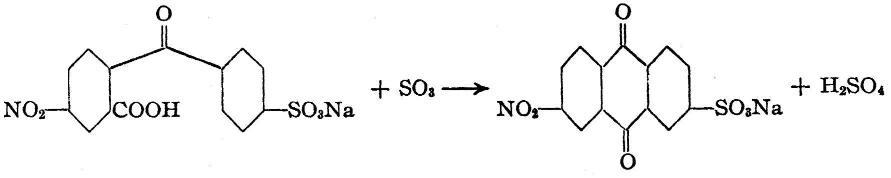
Several new 4'-sulfo-o benzoylbenzoic acid derivatives and the corresponding anthraquinone compounds are described. They are, 4'-sulfo-2-benzoyl-5-nitrobenzoic acid, 2-nitroanthraquinone-7-sulfonic acid, 2-nitro-7-chloroanthraquinone, 2-amino-7-chloroanthraquinone, 4'-sulfo-2-benzoyl-5-aminobenzoic acid, 2-aminoanthraquinone-7-sulfonic acid, 2,7-diaminoanthraquinone.

In the synthesis of anthraquinone derivatives from 4'-sulfo-o-benzoylbenzoic acid, a very interesting series of new compounds has been studied.

When 4'-sulfo-o-benzoylbenzoic acid is nitrated the nitro group enters the benzoic acid ring, not the sulfo benzene ring, as expected. The main product formed is 4'-sulfo-2-benzoyl-5-nitrobenzoic acid.



4'-Sulfo-2-benzoyl-5-nitrobenzoic acid is soluble in concentrated sulfuric acid and on heating the solution the ring closes to form 2-nitroanthraquinone-7-sulfonic acid.



By treating 2-nitroanthraquinone-7-sulfonic acid with sodium chlorate in dilute acid solution, the sulfonic acid group is replaced by chlorine and 2-nitro-7-chloroanthraquinone is produced quantitatively.

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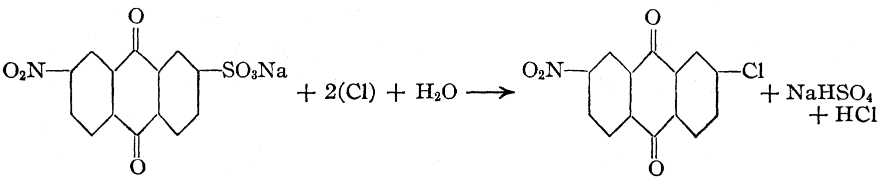
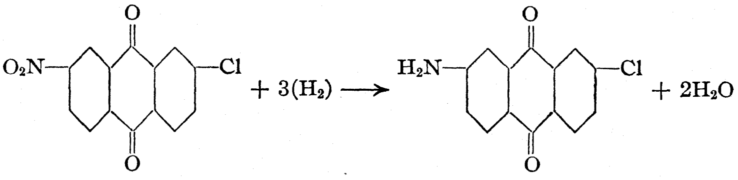
[1] Presented before the Division of Dye Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8–12, 1930, by J. M. **Tinker.**

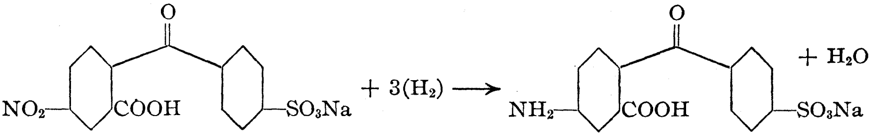


This nitrochloro compound crystallizes from chlorobenzene in light yellow crystals melting at 251 to 252° and has not been described. By reducing the 2-nitro-7-chloroanthraquinone with sodium sulfide, the 2-amino-7-chloroanthraquinone is formed.

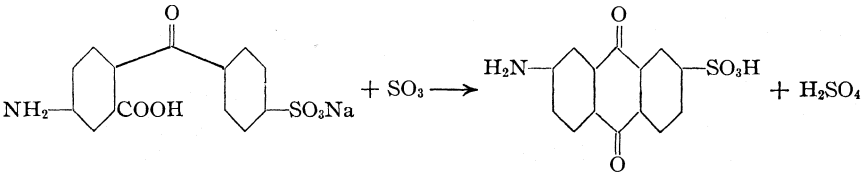


When pure it crystallizes in light orange needles melting at 302 to 303°.

Instead of ring closing 4'-sulfo-5-nitro-2-benzoylbenzoic acid, the nitro group may be first reduced to the 4'-sulfo-2-benzoyl-5-aminobenzoic acid.



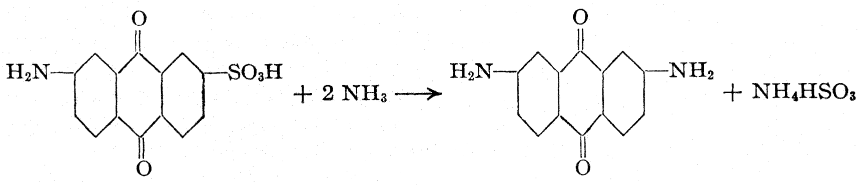
This amino compound analyzes 99.8% by nitrite titration based on a molecular weight corresponding to the formula above and on ring closing this amino compound with sulfuric acid, the 2-amino-anthraquinone-7-sulfonic acid is formed.



This product corresponds to the 2-aminoanthraquinone-7-sulfonic acid described by F. Kaufler,[2] obtained from the 2,7-anthraquinone-disulfo acid by amination.

By treating this aminoanthraquinone-sulfo acid with ammonia and arsenic acid, the well-known 2,7-diaminoanthraquinone is produced.

[2] F. Kaufler, *Ann.*, *351*, 158 (1907).



This diaminoanthraquinone is easily recrystallized from nitrobenzene, giving dark violet crystals melting at **330** to 332°. On conversion to the dioxy derivative by the Sandmeyer method, a dioxy body is formed melting above 340°. On acetylation a diacetyldioxyanthraquinone is formed which melts at 190 to 191°.

E. Noelting and W. Wortmann[3] describe a diaminoanthraquinone obtained from 2,7-dinitroanthraquinone, which is the same in properties as the one obtained by this synthesis.

Compound	M. p., °C.	Compound M. p., °C.
2,7-Dioxy-anthraquinone	Over 330	Diacetyl 190 to 191
2,6-Dioxy-anthraquinone	Over 330	Diacetyl 228 to 229
2,3-Dioxy-anthraquinone	Over 260	Diacetyl 203 to 205
1,7-Dioxy-anthraquinone	Over 292 to 293	Diacetyl 198 to 199
1,8-Dioxy-anthraquinone	Over 191	Diacetyl 227 to 232
1,6-Dioxy-anthraquinone	Over 276	Diacetyl 204 to 205
1.5-Dioxy-anthraquinone	Over 280	Diacetyl 244 to 245
1,4-Dioxy-anthraquinone	Over 194 to 195	Diacetyl 200
1,3-Dioxy-anthraquinone	Over 270	Diacetyl 183 to 184
1,2-Dioxy-anthraquinone	Over 289 to 290	Diacetyl 184
Unknown dioxy-anthraquinone	Over 330	Diacetyl 190 to 191

Experimental Part

(1) Preparation of **4′-Sulfo-2-benzoyl-5′-nitrobenzoic** acid, Monosodium **Salt.**—Dissolve 328 g. of 4'-sulfo-o-benzoylbenzoic acid monosodium salt in 650 parts of 100% sulfuric acid at 15 to 20". While agitating, add over a period of six to eight hours, 580 g. of mixed acid (made by mixing 100 g. of mixed acid containing 70% nitric acid, 22% sulfuric acid and 8% water with 480 parts of 25% oleum). Hold the temperature at 15 to 20° during the addition, then raise to 35° and hold for three hours.

Dilute the finished nitration by pouring onto 2500 g. of ice and 1500 g. of water, then salt out the 4'-sulfo-2-benzoyl-5-nitrobenzoic acid monosodium salt with 1000 g. of salt. Filter after a few hours, wash with cold water and dry (weight 350 g.). It is a white crystalline powder easily soluble in water to a pale yellow solution. With alkalies it forms the diacid salts, which are very soluble in water. It is difficultly soluble in cold alcohol and is best purified by crystallizing from a hot dilute sulfuric acid solution.

Anal. Calcd.: S, 8.58; N, 3.75. Found: S, 8.49; N, 3.70.

(2) Preparation of 2-Nitroanthraquinone-7-sulfonic Acid.—Dissolve 100 g. of 4'-sulfo-2-benzoyl-5-nitrobenzoic acid in 400 g. of 25% oleum and heat to 150°. Cool quickly and pour onto 2500 g. of ice. Filter the precipitated 2-nitroanthraquinone-7-sulfonic acid and wash well with cold water. This yield is 80 g.

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[3] Noelting and Wortmann, *Ber.*, 39, 641 (1906).

(3) Preparation of **2-Nitro-7-chloroanthraquinone.**—Suspend 35.5 g. of 2-nitroanthraquinone-7-sulfo acid (sodium salt) in 1750 cc. of water and 90 g. 20° Bé. hydrochloric acid in a five-liter flask with a glass agitator. Heat to boiling and add a solution of 35.5 g. of sodium chlorate dissolved in 500 cc. of water over a period of twenty to twenty-four hours. The volume is kept constant at 2 liters. When finished, filter, wash well with hot water and dry at 100° in vacuum. The yield is quantitative.

The 2-nitro-7-chloroanthraquinone is easily purified by crystallizing from chlorobenzene or glacial acetic acid as light yellow crystals melting at 251 to 252°.

(4) Preparation of **2-Amino-7-chloroanthraquinone.**—287 g. of 2-nitro-7-chloroanthraquinone is suspended in 5 liters of water containing 40 g. of sodium hydroxide and 625 g. of sodium sulfide crystals. Heat to boiling in two to three hours and hold at the boiling point for two hours. The 2-amino-7-chloroanthraquinone is then filtered off and washed well with hot water. The yield is almost quantitative. This body crystallizes easily from chlorobenzene in light orange needles melting at 302 to 303°.

Anal. Calcd. for $C_{14}H_8SO_2NCl$: N, 5.44; Cl, 13.8. Found: N, 5.34; Cl, 14.3.

(5) Preparation of **4′-Sulfo-2-benzoyl-5-aminobenzoic Acid.**—373 g. of 4′-sulfo-2-benzoyl-5-nitrobenzoic acid monosodium salt is suspended in about 300 g. of hot water. Add this mixture in about three to four hours to an agitated mixture of water, 750 g. of powdered iron and 75 g. of glacial acetic acid held at 93 to 97°. Hold for another hour at 95 to 97°, then neutralize with about 175 g. of sodium carbonate. Filter off the iron sludge and wash well with about 1 liter of boiling water. Acidify the mother liquor and wash water with hydrochloric acid, when the 4'-sulfo-2-benzoyl-5-aminobenzoic acid monosodium salt will precipitate and is filtered and washed with cold water. The yield is 300 g. This is a white crystalline product, easily purified by crystallizing from hot water. It is easily soluble in alkalies but sparingly soluble in cold water and dilute mineral acid, 95% alcohol, glacial acetic acid or other organic solvents.

(6) Preparation of **2-Amino-anthraquinone-7-sulfo Acid.**—Dissolve 40 g. of 4′-sulfo-2-benzoyl-5-aminobenzoic acid monosodium salt in 240 g. of a mixture of 87 g. of 66" Bé. acid and 113 g. of 25% oleum, heat to 180° and hold at this temperature for one hour. Pour onto ice, then filter, wash and dry.

(7) Preparation of **2,7-Diaminoanthraquinone.**—Charge a high-pressure steel autoclave with 318 g. of ammonium salt of 2-aminoanthraquinone-7-sulfo acid, 156 g. of arsenic acid and 1860 g. of 27% ammonia and heat for twenty-four hours at 180°.

After cooling, the reaction mass is filtered and washed well. The dried product is red needles melting at 330 to 332°. Further crystallization from nitrobenzene does not change this melting point.

Conclusion

When 4'-sulfo-2-benzoylbenzoic acid is nitrated, the nitro group enters the benzoic acid ring. Proof of structure is based on the melting point of the 2,7-diaminoanthraquinone, as well as the melting point of the 2,7-dioxyanthraquinone and 2,7-diacetyl-dioxyanthraquinone, which are prepared from the sulfo-benzoyl-*o*-benzoic acid. The several intermediate products are described.

MILWAUKEE, WISCONSIN

[CONTRIBUTION FROM THE FOOD RESEARCH INSTITUTE AND DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

NOTE ON THE TER MEULEN–HESLINGA METHODS FOR THE ESTIMATION OF NITROGEN, CARBON AND HYDROGEN IN ORGANIC MATERIAL[1]

BY E. P. GRIFFING AND C. L. ALSBERG

RECEIVED DECEMBER 8, 1930 PUBLISHED MARCH 6, 1931

The purpose of this note is to make the excellent methods of Ter Meulen and Heslinga for the estimation of carbon, hydrogen and nitrogen more generally known in America, and to suggest some slight modifications based on two years' experience in their use. Both methods employ much less material than the customary macro methods without requiring the special equipment or unusual technique of the micro methods in general use.

The Carbon–Hydrogen Method.—This depends upon catalytic oxidation with manganese dioxide. A micro-balance is not necessary, though one with a sensitivity of 0.05 mg. is desirable. If such a balance is not available, the sample to be taken must be larger. With an ordinary analytical balance sensitive to 0.1 mg., the carbon–hydrogen estimation requires fifty to one hundred milligrams and takes one hour.

Several changes in the apparatus set-up recommended by Ter Meulen and Heslinga are suggested. We used compressed commercial oxygen, regulating the velocity of the gas flow by a double-head reduction valve, and introduced a manometer in the line next to the oxygen cylinder to register any resistance to the passage of the products of combustion or to the flow of oxygen that might arise. The oxygen was passed through a purifying train consisting first of sulfuric acid, then of ascarite to absorb carbon dioxide and lastly of dessicite to absorb moisture.

We used a much larger quartz combustion tube than that specified by Ter Meulen and Heslinga, namely 35 cm. long and 10 mm. bore. The additional length permits the use of a copper wire coil between the combustion boat and the end of the tube through which the boat is introduced. Heating this coil to a high temperature by a separate micro-burner during combustion helps to prevent back flow of gases, should there be a sudden increase in pressure. The larger diameter permits the use of more catalyst per unit length, so that it need not be renewed so frequently. A copper wire coil extending the length of the catalyst was found advantageous to prevent the catalyst from becoming too densely packed due to sudden increase in pressure, if combustion was too fast.

Much difficulty was encountered at first in preparing active catalyst.

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[1] H. Ter Meulen and H. Heslinga, Leipzig, 1927; H. Ter Meulen. *Rec. trav. chim.*, 43, 643 (1924); H. Ter Meulen, *ibid.*, 44, 271 (1925).

We adopted the method of Rogers, Piggot, Bahlke and Jennings[2] for preparing manganese dioxide from calcium permanganate. We have found it advantageous in order to increase its density to subject the wet precipitate of manganese dioxide to great pressure in a hand-press before drying on a sand-bath. Catalyst thus prepared is very active and has a very long life. As it becomes exhausted, it changes in color from intense black to rusty black.

In analyzing nitrogenous substances Ter Meulen and Heslinga employ a layer of lead peroxide behind the manganese dioxide to hold back the nitrous oxide. Since the lead peroxide in the powdered form has a tendency to pack in the tube, we used it in granulated form of a 12–20 mesh size.

For absorption of the combustion products very light weight U-tubes were used, so that their loaded weight did not exceed 25 g. Water was absorbed by dessicite, carbon dioxide by ascarite. Behind the ascarite in the carbon dioxide absorption tube a short length of dessicite was used to prevent loss of moisture from this tube. Following the absorption train we found it most advantageous to use a Marriotte flask (aspirator bottle) in order to maintain a uniform, slightly reduced pressure in the absorption train. This can be attained by having the opening of the inlet tube dipping into the water in the bottle 20 mm. above the orifice of the outlet tube.

The method itself is very accurate; the limiting factor is the accuracy of weighing. Therefore, results obtained with an ordinary analytical balance and small samples will prove of interest. Thirteen analyses of sucrose, the average weight of sample being 40 mg., gave an average carbon content of 42.31% as against 42.1% theoretical. The sensitivity of the balance used was such that the variability due to lack of sensitivity of the balance might amount to 0.21% carbon for a 40-mg. sample. Six determinations of the carbon content of oxalic acid, the average weight of sample being 28 mg., gave 19.21% as against 19.05% theoretical. The experimental error that might be due to the weighing was 0.25% carbon. It is obvious, therefore, that if only an ordinary analytical balance is available, somewhat larger samples should be used.

The Nitrogen Method.—This depends upon hydrogenation with a nickel catalyst and titration of the resulting ammonia. Using an ordinary analytical balance we have obtained satisfactory results with as little as 20 mg. of sample. The time required is only thirty minutes.

The following modifications in set-up of apparatus are suggested: instead of heating the catalyst by a gas-burner under an asbestos box, we used an electric furnace for that portion of the quartz tube containing the

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[2] T. H. Rogers, C. S. Piggot, W. H. Bahlke, and J. M. Jennings, THIS JOURNAL, 43, 1973 (1921), Method 5.

catalyst. It is not then necessary to cool down during the day, even when changing the boats; a constant temperature may be maintained. Instead of collecting the ammonia in a solution kept just on the acid side of neutrality by addition from time to time of standard acid from a buret supported over the flask, we found it advantageous to collect it in an excess of acid and to titrate the excess at the end of the combustion, after having boiled the contents to remove carbon dioxide. We also found a 1% solution of alizarin sulfonate to be superior to methyl orange for the titration of the seventieth normal acid which we used. Micro-burets of 5 cc. capacity, with scale divisions of 0.02 cc. which could be estimated to 0.002 cc., were used for the titration.

By this technique we were able to determine total nitrogen in such plant materials as wheat leaves and straw in about 250 samples with an accuracy such that duplicate analyses varied by less than 0.1% of nitrogen and very often by only one or two hundredths per cent. When one considers that it is extremely difficult to secure homogeneity in such small samples of this type of material, the method may well be regarded as extremely satisfactory. The results are more accurate than those we could obtain upon the same material with the customary macro Kjeldahl method.

We regard the method as preferable to the Kjeldahl method wherever only a few determinations a day are to be made, for it is not much more time consuming. It is more accurate and does not require a separate digestion room with special hood to remove the gases of boiling sulfuric acid. If, as is the case in fertilizer and feeding stuffs control laboratories, hundreds of analyses have to be made daily, the Kjeldahl method is more expeditious. Moreover, since the Kjeldahl method employs a very much larger sample, it is to be preferred for inhomogeneous materials like fertilizers and feeding stuffs that are difficult to sample.

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[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, AND THE OFFICE OF HORTICULTURAL CROPS AND DISEASES, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

SOME ORGANIC ACIDS OF WHEAT PLANTS[1]

BY E. K. NELSON[2] AND HEINRICH HASSELBRING[3]

RECEIVED DECEMBER 13, 1930 PUBLISHED MARCH 6, 1931

Many of the constituents of wheat plants have been repeatedly and thoroughly investigated. In Wehmer's book, "Die Pflanzenstoffe," second edition, 1929, mention is found of a considerable number of organic and inorganic constituents. However, the non-volatile organic acids are not mentioned.

In the course of a study on the buffer system of the wheat plant,[4] Hurd-Karrer found that the form of the titration curve between P_H 2.0 and 6.0 suggested the presence of malic acid in the juice, which observation directed attention to the fact that the nature of the organic acids of wheat had not been reported. The present work was accordingly undertaken, in cooperation with the office of Cereal Investigations of the United States Department of Agriculture, to determine the identity and relative amounts of the acids in the tissues of the wheat plant.

The material used for this study was winter wheat grown on the Arlington Experimental Farm at Rosslyn, Virginia, during the season of 1927–1928. Samples were collected from May 15 until May 28, 1928. The plants at this time were in a vigorous state, free from rust and other diseases. When cutting was begun, no heads had appeared, but toward the end of the cutting, heads had begun to show. The plants were cut about four inches or more above the ground so that none of the basal, yellowing leaves were included in the samples.

The material was immediately taken into the laboratory, cut into short pieces in a meat slicer, weighed and thoroughly extracted with boiling water. The total weight of the green plants was 76,054 g., 14,527 g. of which was dry matter.

The liquid was strained through a closely woven bag to which the solid residue was finally transferred. The remaining liquor in the residue was pressed out in a tincture press, and was added to the strained portion.

The liquid portion was treated with successive portions of a saturated solution of basic lead acetate until no precipitate was formed by further addition of lead acetate. The precipitates were collected on Büchner funnels and dried at room temperature. Combined, they amounted to 1715 g.

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[1] Food Research Division Contribution No. 86.

[2] Bureau of Chemistry and Soils.

[3] Bureau of Plant Industry.

[4] Hurd-Karrer, "Titration Curves of Etiolated and of Green Wheat Seedlings Reproduced with Buffer Mixtures," Plant Physiol., 3, 307–328 (1930).

For the separation of the non-volatile acids by the ester distillation method, 685 g. of the lead precipitate was decomposed by sulfuric acid, and filtered from lead sulfate. The excess of sulfuric acid in the filtrate was removed by its exact equivalent of barium hydroxide. The barium sulfate was removed by filtration, and the solution of organic acids was concentrated to small volume, treated with a liberal quantity of absolute alcohol, and filtered from precipitated proteids and extraneous materials

The alcoholic solution was evaporated to dryness and esterified with alcoholic hydrochloric acid (one liter of absolute alcohol containing 25 g. of dry hydrochloric acid). The excess alcohol was evaporated and the esterification repeated. The alcohol was again evaporated and the residue dissolved in ether. Considerable insoluble material was left. The ethereal solution was filtered, shaken with a solution of sodium hydroxide to remove free acids and evaporated. Fifty-two grams of the crude mixed esters were obtained.

The esters were submitted to fractional distillation at **10** mm., and the distillates were re-fractionated at the same pressure.

The results of the fractionation are as follows

		G.
1	90–100° (redistilled at 85–90°)	2.2
2	100–120°	0.1
3	120–125°	.1
4	125–135° (α_D −10.7")	21.0
5	135–145"	1.8
6	145–155°	1.5
7	155–165°	0.6
8	165–170°	13.2
	Residue (oily)	6.8
		47.3

The hydrazides were prepared from these fractions.

Fraction **1** yielded a hydrazide which came down at once in needles. These were in very small quantity and when recrystallized melted at 235°. They agreed in optical properties[5] with oxalic hydrazide.

The filtrate from this hydrazide, on longer standing, yielded another hydrazide, crystallizing in plates, melting after recrystallization at 149–151'. Optical examination confirmed its identity with malonic hydrazide.

The filtrate from malonic hydrazide, on evaporation, yielded a small quantity of an alcohol-soluble hydrazide, melting at 68–75°, which indicated levulinic hydrazide. As levulinic acid may have been formed by the action of alcoholic hydrochloric acid on carbohydrates, it is not considered as originally present in the plant.

Fractions 2 and **3,** being small in quantity, were disregarded.

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[5] Optical crystallographic examinations were made by G. L. Keenan of the Food, Drug and Insecticide Administration.

Fraction 4 yielded a copious precipitate of a hydrazide having the appearance of malic hydrazide. It melted at 178–179°. Admixture with *l*-malic hydrazide caused no depression in the melting point. The optical rotation of this fraction also indicates that it is the ester of *l*-malic acid.

Fractions 5 and 6 also yielded impure malic hydrazide. These fractions were saponified and tested for tartaric acid by the tentative method of the A. O. A. C., with negative results.

Fraction 7 yielded an impure hydrazide which appeared to contain malic and citric hydrazide.

Fraction 8 also yielded a pasty hydrazide which was partly crystalline. As its behavior indicated that it was aconitic acid, a small quantity of the fraction was saponified, acidified and extracted with ether. Aconitic acid was identified in the residue from the ether. Therefore fraction 8 was refractionated. Six grams boiling at 170° at 10 mm. was obtained which afforded a hydrazide melting at 104–105° and agreeing with citric hydrazide in optical properties.

For the separation of aconitic acid, the mixed acids, liberated from 500 g. of the lead precipitate, were dissolved in water and extracted with ether in an apparatus designed for the continuous extraction of liquids with ether until negligible quantities of ether-soluble acids were left in the aqueous liquid. The extracted acids were partly crystalline. They were dissolved in ether, and the ether solution was shaken out with five 5-cc. portions of water. The water solution was diluted and shaken out four times with an equal volume of ether, which was then united with the main ether solution.

The ether was evaporated in a tared beaker, and the residue was dried on a steam-bath at reduced pressure until free from water and volatile acids. It was a solid, crystalline acid, weighing 9.0 g. On recrystallizing from water the acid melted at 183–185°. It decolorized permanganate solutions, gave the acetic anhydride test for aconitic acid, and agreed with that acid in its optical crystallographic properties.

The citric and malic acids were further determined in a portion of the lead precipitate by the tentative methods given in "Methods of Analysis," A. O. A. C., second edition.[6] Citric acid was determined as pentabromoacetone and malic acid by the polariscope method. The figures were somewhat higher than those obtained by the ester distillation method.

Oxalic acid, left in the extracted plants as an insoluble salt, was determined by the Arbenz[7] method.

The percentages of non-volatile acids, calculated on the basis of green wheat plants, were found to be as follows

Malonic acid (by fractionation of esters)	0 005%
Aconitic acid (by ether extraction of acids)	.040%

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[6] These analyses were made by H. H. Mottern of the Food Research Division.

[7] Arbenz, *Mitt. Lebensm. Hyg.*, 8, 98 (1917).

Malic acid (by fractionation of esters)	0.056%
Malic acid (by polarization)	.064%
Citric acid (by fractionation of esters)	.016%
Citric acid (by pentabromoacetone)	.019%
Oxalic acid	Trace
Oxalic acid in residue, dry basis	0.11%
Oxalic acid in residue, fresh basis	.02%

Aconitic acid has been identified previously in two species of the *Gramineae* (sugar cane and sorghum).

Malonic acid has not been found in any of the investigations on the organic acids of fruits, but was reported present in alfalfa by Turner and Hartman.[8]

Summary

In this investigation of the organic acids in growing wheat plants the water extract was found to contain aconitic, citric, malic and malonic acids with a trace of oxalic acid. The residue after water extraction was found to contain oxalic acid.

WASHINGTON, D. C.

[A COMMUNICATION 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. II

BY GEORGE J. PFEIFFER AND HOMER ADKINS

RECEIVED DECEMBER 20, 1930 PUBLISHED MARCH 6, 1931

The reaction of orthoformic ester and ketones to form acetals and ethyl formate (Equation I) is a reversible reaction suited to the study of the relationship of the structure of compounds to the strength of oxygen to carbon linkages.

$$R_2CO + HC(OC_2H_5)_3 \longleftrightarrow R_2C(OC_2H_5)_2 + HCO_2C_2H_5 \qquad (I)$$

Recently the extent of acetal formation for eight ketones was reported.[1] In extending the study of this reaction it became apparent that the previous evaluation of the analytical data was in error in the case of one ketone, so the method of analysis was subjected to a more thorough study.

The analytical method used by Carswell for the determination of the extent of the acetal reaction was based upon the observation of Geuther that ethyl formate in the presence of sodium ethoxide decomposed into carbon monoxide and alcohol. Geuther formulated the reaction as in Equation II.

$$HCO_2C_2H_5 = CO + C_2H_5OH \qquad (II)$$

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[8] Turner and Hartman, THIS JOURNAL, 47, 2044 (1925).

[1] Carswell and Adkins, *ibid.*, 50, 235 (1928).

Geuther did not obtain the theoretical yield of carbon monoxide but accounted for the discrepancy by the assumption that the reaction is reversible. This assumption was based upon the finding that ethanol inhibited the decomposition of the ester. In order to avoid this effect of ethanol upon the decomposition, Carswell carried out the decomposition in the presence of metallic sodium, thus perhaps changing the course of the reaction. Under these conditions he found that the amount of carbon monoxide was 64.4 ± 1.5% of that required by Geuther's equation. More recently in a series of eight consecutive decompositions of ethyl formate the amount of carbon monoxide was found to be 66.1, 66.4, 65.7, 69.4, 63.6, 66.1, 66.6, 62.7, or an average of 65.8% of the amount required by Geuther's equation. That is to say, three moles of ethyl formate gave two moles of carbon monoxide. Moreover, methanol was shown by Trillat's test to be in the residue from the decomposition.[2] Mr. Ralph Dunbar in this Laboratory has recently obtained a mixture of alcohols consisting of 9.5% methanol and 90.5% ethanol as a result of the hydrolysis of the residue from the decomposition of ethyl formate with sodium and an excess of sodium ethoxide. The decomposition of ethyl formate under these conditions may then be formulated as in Equation III. The mechanism will be discussed in a later paper.

$$3HCO_2C_2H_5 + 4Na = 2CO + CH_3ONa + 3C_2H_5ONa \qquad \text{(III)}$$

The ratio of carbon monoxide to ethyl formate was found to be independent of the amount of orthoformic ester or of ketone acetal which may be present in the mixture subjected to analysis. However, the ratio of carbon monoxide to ethyl formate was dependent upon the amount of ethanol and the amount and kind of ketone present in the mixture subjected to analysis. Since the ethanol present before the decomposition of the ethyl formate and formed during the decomposition would be in the form of sodium ethoxide, it may perhaps be better to state that the amount of ethyl formate converted to carbon monoxide was a function of the amount of sodium ethoxide and of the amount and kind of ketone in the reaction mixture. Sodium ethoxide no doubt decreased the amount of ethyl formate converted to carbon monoxide because it facilitated the reaction of ethyl formate with the ketone. These reactions are of at least two types as indicated in Equations **IV** and V. Reaction **IV** is the Claisen reaction, while reaction V is, so far as the authors are aware, a hitherto unknown reaction which will be described in detail in a later publication.

$$HCO_2C_2H_5 + CH_3C(O)CH_3 = C_2H_5OH + CH_3C(O)CH{=}CHOH \qquad \text{(IV)}$$
$$HCO_2C_2H_5 + (C_6H_5)_2CO = (C_6H_5)_2C(OH)CO_2C_2H_5 \qquad \text{(V)}$$

The amount of ethyl formate equivalent to a given volume of carbon monoxide under the conditions of analysis was determined by experi-

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[2] Trillat, *Analyst,* 24, 13, 211 (1899).

ment. Various mixtures containing known amounts of ethyl formate and ethanol, and various kinds and amounts of ketones were therefore subjected to the action of sodium and sodium ethoxide and the amount of carbon monoxide so formed was measured. The sum of the amounts of ester and of ketone in a mixture submitted to analysis was always 0.1 of a mole since that ratio would exist in the reaction mixtures which were to be analyzed. These prepared mixtures were made up to a volume of 50 ml. with dry toluene. A 5-ml. aliquot was taken from each and treated with 0.5 g. of sodium ethoxide and an excess of sodium, and subjected to decomposition at 110 to 115°. There are given in Table I the data obtained in a group of such analyses.

TABLE I

Carbon Monoxide (in Moles × 10^3) from Ethyl Formate in the Presence of Various Amounts of Ethanol and Ketones

Ketones		Ester, moles	Ethanol, ml			
Name	Moles		8	16	24	32
Dimethyl	0.02	0.08	19.40	19.30	18.30	17.80
	.005	.095	46.70	44.50	42.40	41.60
Methyl ethyl	.09	.01	1.50	1.24	1.17	0.95
	.07	.03	3.30	3.34	3.00	2.90
	.05	.05	4.84	4.28	4.35	4.27
	.03	.07	8.75	8.65	7.60	7.38
	.01	.09	41.50	39.70	38.00	35.00
	.005	.095	47.30	47.00	44.00	41.00
Methyl β-phenyl ethyl	.03	.07	8.15	8.15	7.15	6.55
	.01	.09	41.30	40.30	37.50	36.60
Methyl phenyl	.09	.01	1.59	1.46	1.13	0.53
	.07	.03	3.12	2.70	2.13	1.46
	.05	.05	6.76	5.61	4.67	3.06
	.03	.07	12.70	8.48	6.31	5.30
	.02	.08	26.00	23.10	19.10	14.50
	.01	.09	43.50	39.00	36.30	32.00
Methyl neopentyl	.03	.07	14.30	10.40	9.75	8.30
	.01	.09	36.00	31.60	28.60	26.80
Di-isopropyl	.05	.05	11.20	11.10	9.70	9.20
	.03	.07	21.00	19.60	17.90	17.50
Methyl *tert.*-butyl	.09	.01	4.20	4.90	4.07	2.93
	.07	.03	7.80	6.75	6.52	6.06
	.05	.05	8.60	7.73	7.42	6.48
	.03	.07	30.40	25.90	22.10	18.20
	.01	.09	43.50	38.40	38.50	32.70
Ethyl *tert.*-butyl	.08	.02	4.95	4.23	3.82	3.44
	.06	.04	12.90	12.40	12.40	10.70
Diphenyl	.08	.02	4.70	3.80	2.70	2.90
	.05	.05	11.60	10.95	9.28	9.28
Isopropyl *tert.*-butyl	.09	.01	1.96	1.85	1.75	1.19
	.07	.03	8.73	8.10	7.08	6.80

The reaction of the various ketones with orthoformic ester was carried out by mixing 0.1 mole of the ketone and 0.1 mole of orthoformic ester in enough dry ethanol to give a total volume of 49 ml., and then after the mixture was at 25°, adding 1 ml. of an ethanol solution containing 0.0136 g. of hydrogen chloride. After fifty to sixty hours 5-ml. aliquots were removed and decomposed with sodium and sodium ethoxide as previously described. The evolved gas was collected and analyzed and the amount of carbon monoxide calculated. The amounts of carbon monoxide formed from the various reaction mixtures are recorded in Column 3 of Table II. Duplicate syntheses of acetal and duplicate analyses of the reaction mixture were made and the variation in the amount of carbon monoxide found is indicated in the table. The amount of ethyl formate required to produce the amount of carbon monoxide actually obtained in the decomposition of an aliquot from an acetal reaction mixture, in the concentration of ethanol given in Column 2 of Table II, may then be determined from the data given in Table I. In order to facilitate this determination the relationship of ethanol and ethyl formate to the amount of carbon monoxide produced in the presence of the various concentrations of each ketone was plotted and the amount of ethyl formate equivalent to a given amount of carbon monoxide read off directly, usually without extensive interpolation from the experimental values. The amount of ethyl formate so calculated is given in Column 4 of Table II. From this value the percentage conversion of the ketone to the acetal and the equilibrium constant are readily calculated.

TABLE II

EXTENT OF ACETAL FORMATION IN REACTION OF 0.1 MOLE OF ORTHORORMIC ESTER WITH 0.1 MOLE OF VARIOUS KETONES IN A SOLUTION MADE UP TO 50 ML. WITH ETHANOL

Ketone	Ethanol, ml.	CO, mole	HCOOEt, mole	% Acetal, calcd.	$K_E \times 10^2$
Dimethyl	24.5	0.0426 ± 4	0.0948	94.8	3.34
Methyl ethyl	25.3	.0375 ± 5	.0901	90.1	0 83
Methyl β-phenylethyl	19.2	.0377 ± 10	.0891	89.1 (88 9)	.66
Methyl phenyl	22.0	.0302 ± 5	.0862	86.2 (85.1)	.39
Methyl neopentyl	18.0	.0257 ± 7	.0840	84.0	.28
Di-isopropyl	19.5	.0173 ± 3	.0654	65.4	.034
Methyl *tert.*-butyl	17.5	.0081 ± 2	.0501	50.1 (52.9)	.0101
Ethyl *tert.*-butyl	20.8	.0106 ± 2	.0362	36.2	.0033
Diphenyl	19 0	.0052 ± 1	.0337	33.7	.0026
Tert.-butyl isopropyl	18.2	.0067 ± 2	.0258	25.8	.0012
Di-*tert.*-butyl	17.0	.0036 ± 2	.0172	17.2	.0004

The equilibrium point in the acetal reaction was also arrived at from the reaction of ethyl formate with an acetal of three of the ketones. One tenth mole each of the acetal and of the ethyl formate was made up to a volume of 49 ml. with dry ethanol and 1 ml. of ethanol containing 0.0136 g.

of hydrogen chloride was added. After the reaction had proceeded for several days, the ethyl formate in an aliquot was decomposed and the amount of carbon monoxide, ethyl formate and percentage conversion to the acetal calculated as in the synthesis of the acetal. The results are given in parentheses in Table II, for the three ketones involved.

An inspection of the values given in Table II for the percentage conversion of various ketones to their acetals makes it clear that any substitution in the methyl groups in acetone results in a lowering of the extent of the reaction. The extent of conversion is decreased only slightly by the substitution of a benzyl group for one of the hydrogens of acetone. The effect of the replacement of a methyl group in acetone by a phenyl group is marked but much less so than might be expected from the differences between methyl and phenyl in most reactions. In contrast with this observation is the fact that two phenyl groups reduce the percentage conversion to acetal to about one-third of the value for acetone. The replacement of a methyl group in acetone by the tertiary butyl group results in a decrease in conversion to the acetal from 94.8 to 50.1%. If the tertiary butyl group is separated from the carbonyl group by one carbon atom it is much less effective in decreasing the extent of the acetal reaction.

The replacement of both methyl groups in acetone by isopropyl groups is also very effective in reducing the percentage conversion to an acetal although not so effective as is one tertiary butyl group. This is further evident from a comparison of the symmetrical and unsymmetrical tetramethyl acetone as the former shows 65.4% conversion to the acetal while the latter is but 36.2%. A further substitution of methyl groups in acetone results in marked lowerings of the percentage conversion to the acetal. The percentage conversion of the ketone to the acetal decreased by about 30% of the former value each time one of the hydrogens in methyl tertiary butyl ketone was replaced by a methyl group. It should be noted that in the case of acetophenone and pinacolone the extent of conversion to the acetal is considerably higher than that previously reported.

Preparation and Purity of Reagents.—Benzyl acetone was prepared in 96% yield by the hydrogenation of benzal acetone at 65° under a pressure of 135 atmospheres of hydrogen over a nickel catalyst. Di-isopropyl ketone was obtained in 10 to 11% yield by the decomposition of calcium isobutyrate at 500°. Some of it was also purchased from Poulenc-Frères (Paris). Methyl neopentyl ketone was prepared as previously described.[3] The two tetramethyl, the pentamethyl and the hexamethyl acetones were prepared by the Haller and Bauer[4] method involving the use of sodamide, methyl iodide and the appropriate ketone. Their directions were followed except that in the prepara-

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[3] McCubbin and Adkins, THIS JOURNAL, 52, 2547 (1930).

[4] Haller and Bauer, *Vog'l* Erd. *Acad. Sciences,* **149, 5** (1909); *Chem. Centr.*, **1910,** 1589.

tion of hexamethyl acetone it was found necessary to carry out the methylation at 115° in a sealed tube rather than under a reflux. The acetal of acetophenone was prepared by allowing 60 g. of acetophenone to react for twenty-four hours at 25° with 100 g. of orthoformic ester in the presence of 50 g. of ethanol and 0.0136 g. of hydrogen chloride. The mixture was then made alkaline by the addition of a few drops of an anhydrous ethanol solution of sodium ethoxide and fractionated. The yield was 73% of the theoretical. The other acetals were prepared in a similar manner. The other reagents used were prepared or purified by the standard methods. The reagents had the physical constants noted in Table III.

TABLE III

PHYSICAL CONSTANTS OF REAGENTS

Name of compound	Boiling point, °C.	d^{25}_{25}
Acetone	56.2–56.7	0.7973
Acetophenone	200–202 (m. p. 20°)	1.029
Benzophenone	156–158 (15 mm.) (m. p. 48°)	....
Benzyl acetone	130–133	1.0079
Di-isopropyl ketone	123–126	0.8021
Methyl ethyl ketone	79–81	.8065
Methyl neopentyl ketone	123–126	.8036
Orthoformic ester	144–146	.9278
Pinacolone	104–107	.8067
Ethyl *tert.*-butyl ketone	123–126	.8017
Tert.-butyl isopropyl ketone	133–134	.8067
Di-*tert.*-butyl ketone	149–151	.8107
Dimethyl acetal of acetophenone	110–112 (16 mm.)	1.0097
Diethyl acetal of pinacolone	52–55 (30 mm.)	0.8446
Diethyl acetal of benzyl acetone	128–132 (8 mm.)	1.0242
Diethyl acetal methyl neopentyl ketone	55–58 (30 mm.)	0.8297
Ethyl formate	54–54.5	.9250

Summary

The extent of conversion of eleven ketones to their acetals through their reaction with orthoformic ester has been determined. This has necessitated a rather extensive experimental investigation of the extent of reaction of various amounts of ten ketones with ethyl formate in the presence of various amounts of sodium ethoxide.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OR WASHINGTON]

A STUDY OF THE CONDENSATION BETWEEN ALIPHATIC ESTERS AND KETONES[1]

BY S. G. POWELL AND KEITH M. SEYMOUR

RECEIVED DECEMBER 22, 1930 PUBLISHED MARCH 6, 1931

The condensation between ketones and esters has long served as a method for obtaining 1,3-diketones. In the case of unsymmetrical ketones the reaction can take place in either of two ways, and it has been found[2] that ketones of the type CH_3COCH_2R react through the methyl rather than the methylene group. This is not what might be expected from the fact that the reaction between 2-butanone and aldehydes[3] indicates the methylene as the more reactive group. That a methylene group is capable of reacting with esters was shown by Morgan, Drew and Porter,' who obtained diketones from 3-pentanone and from 4-heptanone. The same authors found that in the case of ethyl acetate and 3-pentanone the product was the expected 3-methyl-2,4-hexanedione when the reaction mixture was not heated, but was 2,4-hexanedione if the standard procedure was followed.

The 2,4-hexanedione apparently results from a reaction between the ethyl acetate and 2-butanone formed by alcoholysis of the 3-methyl-2,4-hexanedione.

In view of the above it seemed possible that under certain conditions ketones of the type CH_3COCH_2R might react through the methylene group and that, if alcoholysis could be prevented, the resulting diketones might be isolated. In none of the cases studied in this investigation was any evidence found that such a reaction occurred.

TABLE I

EXPERIMENTAL RESULTS

No.	Ester	Ketone	Diketone	Yield, %
1	Ethyl acetate	2-Butanone	2,4-Hexanedione	11
2	Ethyl propionate	Acetone	2,4-Hexanedione	15
3	Ethyl propionate	2-Pentanone	3,5-Octanedione	9
4	Ethyl butyrate	2-Butanone	3,5-Octanedione	..
5	Ethyl acetate	3-Methyl-2-butanone	2-Methyl3.5-hexanedione	14
6	Ethyl isobutyrate	Acetone	2-Methyl-3,5-hexanedione	6

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[1] Presented at the Cincinnati Meeting of the American Chemical Society, September, 1930. This paper is taken from a thesis submitted by Keith M. Seymour in partial fulfilment of the requirements for the degree of Master of Science in the University of Washington.

[2] (a) Claisen and Ehrhardt, *Ber.*, 22, 1009 (1889); (b) Morgan and Reeves, *J. Chem. Soc.*, 123,444 (1923); (c) Morgan and Drew, *ibid.*, 125,731 (1924); (d) Morgan and Holmes, *ibid.*, 127,2891 (1925).

[3] Zalkind, *J. Russ. Phys.-Chem. Soc.*, 37, 484 (1905); *Chem. Zentr.*, 82, II, 752 (1905); Merling and Kohler, U. S. Pat. 981,668, *Chem. Abstracts,* 5, 1192 (1911); Powell, THIS JOURNAL, 46,2514 (1924).

[4] Morgan, Drew and Porter, Ber., 58,338 (1925).

The course of the reaction when the standard procedure was followed was determined by preparing a diketone by two different ester–ketone combinations such that the identical product would be obtained if the reaction took place through the methyl group. The results are shown in Table I.

Of the three diketones obtained, 2,4-hexanedione and 3,5-octanedione have been previously prepared by reactions 1 and 4, respectively, whereas 2-methyl-3,5-hexanedione has not heretofore been prepared by the Claisen reaction, although obtained by other methods.[5]

The reaction was carried out as described by Claisen and Ehrhardt,[6] and by modifications of this method. Wherever the work was a repetition of that of others, our results were identical with theirs and are not described. According to the standard procedure as described by Claisen and Ehrhardt, the reaction mixture is allowed to stand for twelve hours and then refluxed for one hour. Since it has been shown that heating brings about alcoholysis in the case of the reaction between ethyl acetate and 3-pentanone, reactions 3, 4 and 5 (Table I) were repeated omitting the refluxing. In no case was there any evidence of the presence of any other diketone than the one resulting from the reaction between the ester and the methyl group of the ketone. Nor did omitting the refluxing in the reaction between ethyl acetate and 2-pentanone and between ethyl propionate and 2-butanone lead to any different results than those obtained by other investigators who used the standard procedure.

Reaction 1 (Table I) was repeated, changing the time of standing before refluxing from twelve hours to three hours in one case and to forty-eight hours in another. The sole effect seemed to be a diminution of the yield.

As reactions 2, 3, 5 and 6 have not been described heretofore, the results obtained in these cases are given. Unless otherwise stated all reactions were carried out using 0.5 atom of sodium, 0.5 mole of ketone and 1.0 mole of ester,[7] and following the standard procedure.

Ethyl Propionate + Acetone.—Diketone, b. p. 150–158°; $n_D^{24.5}$ 1.4505. Copper salt, m. p. 197°. 2,4-Hexanedione boils at 158° and its copper salt melts at 197–198°.[8] A second trial using 1 mole of acetone also gave 2,4-hexanedione in much smaller yield.

Ethyl Propionate + 2-Pentanone.—Refluxing omitted; diketone, b. p. 187–190°; $n_D^{24.5}$ 1.457. Copper salt, m. p. 157–158". 3,5-Octanedione boils at 189–190° and its copper salt melts at 157°.[9]

Ethyl Acetate + 3-Methyl-2-butanone.—Twenty-five grams (0.3 mole) of the ketone, 7 g. (0.3 atom) of sodium and 26 g. (0.3 mole) of ester were used. No reaction

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[5] (a) Conrad and Gast, *Ber.*, 31, 1339 (1898); (b) Bouveault, *Compt. rend.*, 131, 45 (1900).

[6] Claisen and Ehrhardt, *Ber.*, 22, 1009 (1889).

[7] Adkms, Kutz and Coffman, THIS JOURNAL, 52, 3218 (1930), have shown that the maximum yields are obtained by using sodium, ketone and ester in the molecular ratio 2:1:3.

[8] Morgan and Reeves, *J. Chem. Soc.*, 123,444 (1923).

[9] Morgan and Drew, *ibid.*, 125, 731 (1924).

took place at 0" and it was slow at room temperature. Refluxing was omitted. Diketone, b. p. 164–166°; copper salt, **m.** p. 172°. 2-Methyl-3,5-hexanedione boils at 160–170" and its copper salt melts at **171**°.[10]

Ethyl Isobutyrate + Acetone.—One-half mole of ester, ketone and sodium were used. The reaction was vigorous but only a small quantity of the copper salt melting at **171**° was obtained. **A** mixture of this with that obtained in the preceding reaction also melted at 171°.

Summary

1. The Claisen condensation between several esters and ketones has been studied and the diketones resulting have been identified.
2. Modifications of proportions and conditions did not change the course of the reaction in the cases studied.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

BROMINE DERIVATIVES OF CERTAIN MIXED ETHERS AND SOME OF THEIR REACTIONS

BY L. CHAS. RAIFORD AND LOUIS H. HOWLAND

RECEIVED DECEMBER 23, 1930 PUBLISHED MARCH 6, 1931

Previous work[1] in this Laboratory has shown that in the bromination of certain phenyl alkyl ethers the hydrogen bromide liberated may split them unless sodium acetate is present, and that the splitting is more pronounced when the alkyl radical is connected through a secondary or tertiary[2] carbon atom.

In cases where, as indicated below, the phenyl radical could not be further brominated under the conditions already described, and where, in consequence of this, no "nascent hydrogen bromide"[3] was produced during attempts at bromination, splitting of these ethers was not observed. Nevertheless, it was a matter of interest to test the behavior of such ethers toward hydrogen bromide under several conditions.

Graebe and Martz[4] found that heating trimethoxygallic acid with 48% hydrobromic acid in an open vessel surrounded by boiling water removed the methyl radical from position 4 to the extent of 90%. In the present work that method did not give satisfactory results. Refluxing 2,4,6-

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[10] Conrad and Gast, **Ber., 31, 1339 (1898).**

[1] Raiford and Birosel, THIS **JOURNAL, 51, 1776 (1929).**

[2] In the tertiary butyl derivative splitting occurred although sodium acetate was present. This may be due to a tendency of the ether to split off the unsaturated hydrocarbon isobutylene. Konowalow [*Z. physik. Chem.*, **1,** 67 **(1887)**] observed such a change in the study of tertiary amyl acetate.

[3] The small amount, if any, produced by the action of bromine on the alkyl radical of the ether was not detected and was disregarded.

[4] Graebe and Martz, *Ann.*, 340, 220 (1905).

tribromophenyl isobutyl and isoamyl ethers with constant boiling hydrobromic acid over a free flame for three and fourteen hours, respectively, caused splitting to the extent of 5 and 12%, while the pentabromo compounds were not affected. These low yields suggested the use of "nascent" hydrogen bromide. Its action was tested in different ways, and examination of Table II (see Experimental Part) will show that the most pronounced effect was obtained by the action of the bromide at an elevated temperature.

In the present work an attempt was made to brominate 2,4,6-tribromophenyl-β,γ-dibromo n-propyl ether[5] with pure bromine, catalyzed by aluminum bromide,[6] in order to secure the corresponding pentabromophenyl derivative. The ether was split and pentabromophenol was obtained. The action was found to be general[7] for the ethers here studied, as indicated in tabular form below.

In previous work it was noted that treatment of phenyl allyl ether with an excess of bromine saturated the aliphatic radical and introduced but two atoms of bromine into the phenyl nucleus, and that these took positions 2 and 4. The structure of this tetrabromo derivative was proved by bromination of 2,4-dibromophenyl allyl ether which, in turn, had been prepared from 2,4-dibromophenol. In the present work this conclusion has been confirmed by further examination of the above indicated tetrabromo compound, and by the study of other similar cases. Thus, the 2,4-dichloro, 2,6- and 3,5-dibromophenyl allyl ethers were treated at 0° in the presence of sodium acetate with a chloroform solution of bromine (1:1 by volume), in excess of that required to saturate the allyl radical and to substitute all available positions in the phenyl group, after which the mixture was allowed to stand at room temperature for about a week. In the first two cases the side chain only reacted, while in the last one both side chain and nucleus were attacked, although the latter was substituted by only two bromine atoms. These results tend to show that in the phenyl allyl ethers when any two of the *o,o,p*-positions have been substituted by bromine no more can be introduced by the method here used.

Claisen[8] found that the allyl ethers of many phenols were readily rearranged by heat, in almost quantitative yield, into the corresponding allylphenols, in which the allyl radical enters the ortho or para position. In subsequent work[9] *p*-bromophenyl and 2,4-dichlorophenyl allyl ethers

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[5] Raiford and Birosel, THIS JOURNAL, 51, 1778 (1929).

[6] Pfeiffer and Haack [*Ann.*, 460, 170 (1928)] found that certain aryl methyl ethers form addition products (molecular compounds) with aluminum bromide, and that these compounds were demethylated by heating for several hours in presence of benzene.

[7] In many cases the pentabromophenol was mixed with a brown powder that could not be identified. The amount formed was greater at boiling point than at room temperature.

[8] Claisen, *Ber.*, 45, 3157 (1912).

[9] Claisen, *Ann.*, 418, 84 (1919)

were found to rearrange. In the present work a small yield of the phenol was obtained from the 2,4-dichlorophenyl derivative, but attempts to rearrange the dibromo compounds were unsuccessful. Likewise, the phenyl alkyl ethers failed to rearrange.

The β,γ-dihalogenated products shaw a number of interesting properties. All of them absorb moisture from the air so rapidly and to such an extent that samples for analyses cannot safely be weighed in open vessels. They also hold alcohol strongly, and those crystallized from this liquid were dried under reduced pressure at elevated temperatures over extra long periods of time to secure samples for analyses.[10] The compounds were further characterized by a study of their behavior toward alcoholic potash. In each case the elements of hydrogen bromide were removed from the side chain, and the corresponding propargyl ether was obtained in nearly quantitative yield. These ethers showed the characteristic properties of acetylene derivatives in the formation of unstable cuprous, mercuric and silver salts, the latter of which were isolated in combination with one molecular proportion of silver nitrate

Experimental Part

The phenyl alkyl ethers indicated below were prepared by Claisen's method,[11] from phenol and the required alkyl halide. The product was then extracted with a solution of caustic alkali to remove phenol, and the ether purified in a suitable way. The tribromo derivatives were obtained by treatment of the ethers with an excess of bromine in chloroform solution,[12] in the presence of sodium acetate. The behavior of these products toward hydrogen bromide is shown in tabular form below.

Preparation of Pentabromophenyl Ethers.—The pentabromophenol used as starting material was prepared by Bodroux's[13] method, modified as follows. One molecular proportion of melted phenol was dropped slowly with stirring into 1.5 times the theoretical amount of bromine in which about 1% aluminum had been dissolved, and the mixture was allowed to stand for twenty-four hours. Unchanged bromine and aluminum salt were extracted by hydrochloric acid solution of potassium bromide, and the phenol by 10% solution of sodium hydroxide. The product was crystallized from benzene or carbon tetrachloride.

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[10] The tendency to absorb alcohol raised the question of the replacement of halogen by the alkoxy radical, as observed by Hell and Gunthert [*J. prakt. Chew.*, *52*, 195 (1895)]. The products of the present work were repeatedly boiled with alcohol without change in composition.

[11] Claisen and Eisleb, *Ann.*, 401, *36* (1913).

[12] When a mixture of 2,4,6-tribromophenyl n-propyl ether and more than five times its weight of pure bromine was allowed to stand in an open Erlenmeyer flask for three days at room temperature, a small yield of tetrabromo derivative was obtained. Failure to lose bromine when treated with alcoholic potash indicated that the halogen was not in the alkyl group. *Anal.* Subs., 0.2708: AgBr, 0.4526. Calcd. for $C_9H_8OBr_4$: Br, 70.79. Found: Br, 71.02.

[13] Bodroux, *Bull. soc. chim.*, [3] *19*, 756 (1898).

The alkyl ethers of pentabromophenol were prepared by Claisen's methods (with the exceptions noted in the table) with the modification that excess of alkyl halide was used. No reaction was obtained with tertiary butyl nor with tertiary amyl halide.

TABLE I

PENTABROMOPHENYL ALKYL ETHERS[a]

	Alkyl	Formula	Crystal form	Yield, %	M. p., ° C.	Halogen,[e] % Calcd.	Halogen,[e] % Found
1	Isopropyl	$C_9H_7OBr_5$	Short needles[d]	Nearly quant.	86	75.47	75.38
2	*n*-Butyl[b]	$C_{10}H_9OBr_5$	Irreg. plates[d]	Nearly quant.	79–80	73.39	73.26
3	Isobutyl	$C_{10}H_9OBr_5$	Short needles[d]	45	92–93	73.39	73.30
4	*Sec.*-butyl[b]	$C_{10}H_9OBr_5$	Fibrous masses[d]	25	57–58	73.39	73.34
5	Isoamyl[c]	$C_{11}H_{11}OBr_5$	Fine needles[d]	Nearly quant.	64–65	71.55	72.68

[a] The methyl, ethyl and n-propyl ethers of this series were obtained by Bonneaud [Bull. *soc. chim.*, [4] 7, 777 (1910)] by the action of the potassium salt of pentabromophenol on the required alkyl halide. No higher yield than 22% was recorded and the ethyl compound contained 1.32% more bromine than calculated. Lucas and Kemp [THIS JOURNAL, **43**, 1661 (1921)] reported an 80% yield of this product from the action of the moist pink silver salt of pentabromophenol on ethyl iodide. Derivatives containing tertiary alkyl radicals have not yet been obtained. [b] The Claisen method was here modified to the extent of adding sodium iodide as well as the required alkyl bromide. Cf. Raiford and Colbert, *ibid.*, 48, 2658 (1926). [c] Obtained by refluxing an aqueous potassium hydroxide solution of the phenol with the required alkyl halide. [d] Crystallized from ligroin (80–100°). [e] Brown and Beal, THIS JOURNAL, **45**, 1291 (1923).

Methods of Splitting the Ethers

1. A glacial acetic acid solution of the ether and phosphorus tribromide to which the calculated amount of water was gradually added was heated under a return condenser.

2. The mixture indicated in 1 was heated in a sealed tube at 135–150° for twelve to fifteen hours. The phosphorus tribromide was contained in an inner tube and did not come in contact with the remainder of the mixture until after the outer tube was sealed.

3. Bromine was dropped into a benzene solution of the ether in which some iodine was present as a catalyst.

4. A mixture of the ether, excess of bromine and about 1% of aluminum in the form of bromide was allowed to stand at room temperature for two days.

The products isolated in these experiments were tribromo- and pentabromophenol, respectively. No attempt was made here to recover any aliphatic halogenated product that might have been formed.

TABLE II

SPLITTING OF TRI- AND PENTABROMOPHENYL ALKYL ETHERS TO GIVE PHENOLS

	Methods			
Ether	1	2	3	4 Phenol, %
	Tribromo Derivatives			
Methyl	No reaction	Completely		
Ethyl	No reaction	Completely		
n-Propyl	No reaction	Completely		
Isopropyl	Completely	....	Completely	
Sec.-butyl	Completely	....	Completely	
Isobutyl	No reaction	Completely		
Isoamyl	No reaction	Completely		

TABLE II (Concluded)

Ether	Methods			
	1	2	3	4 Phenol, %
	Pentabromo derivatives			
Methyl	....	Completely	No reaction	80"
Ethyl	....	Completely	No reaction	40"
n-Propyl	....	Completely		40"
Isopropyl[b]	Completely	....	No reaction	60"
n-butyl	....	Completely		30"
Isohutyl	....	Completely		20[a]
Sec.-butyl[b]	Completely	....		70"
Isoamyl	....	Completely		30[a]

[a] The pentabromophenol was mixed with a brown amorphous solid that was not identified. Treatment at the boiling point of the mixture gave a lower yield of phenol and in some cases a larger quantity of the brown solid, which possibly was formed from the phenol.

[b] Split by boiling with bromine in the absence of aluminum bromide to give high yields of pentabromophenol and some resinous material.

Substituted Phenyl Allyl Ethers

2,4-Dichlorophenyl Allyl Ether.—This was obtained by treatment of the corresponding dichlorophenol in acetone solution with potassium carbonate and with excess of allyl bromide by Claisen's[14] general method. The product distilled as an almost colorless oil at 144–145° and 25 mm.

Anal. Subs., 0.2821: AgCl, 0.3988. Calcd. for $C_9H_8OCl_2$: Cl, 34.97. Found: Cl, 34.95.

3,5-Dibromophenyl Allyl Ether.—When the required phenol[15] was treated with allyl bromide as indicated above an almost quantitative yield of ether was obtained: b. p. 145° at 10 mm.

Anal. Subs., 0.2970: 20.4 cc. 0.1 *N* $AgNO_3$. Calcd. for $C_9H_8OBr_2$: Br, 54.79. Found: Br, 54.73.

2,6-Dibromophenyl Allyl Ether.—2,6-Dibromo-4-nitrophenol was reduced as directed by Mohlau and Uhlmann,[16] and the amino group replaced by hydrogen as follows. One-third of a molecular proportion of the amino compound was dissolved in a mixture of 750 cc. of 95% alcohol and 100 cc. of benzene, after which 50 cc. of concentrated sulfuric acid was added slowly with shaking. This mixture was placed in a suitable flask bearing a Y-tube, one arm of which was connected to a reflux condenser, while the other served for the introduction of sodium nitrite. Fifty grams of the finely powdered salt was slowly added. After reaction was apparently over, the mixture was refluxed for two hours, and then allowed to stand in a warm place for several hours. The product obtained by steam distillation and crystallization from dilute alcohol agrees in properties with that described in the literature. By treatment with excess of allyl bromide it was converted into the ether, which distilled at 132–133° at 10 mm.

Anal. Subs., 0.3423: 23.44 cc. 0.1 N $AgNO_3$. Calcd. for $C_9H_8OBr_2$: Br, 54.79. Found: Br, 54.74.

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[14] Claisen and Eisleb, Ann., 401, 36 (1913).

[15] This was prepared from pentabromophenol by Kohn and Fink's [*Monatsh.*, 44, 188 (1923)] method

[16] Mohlau and Uhlmann, Ann., 289, 94 (1896).

Pentabromophenyl Allyl Ether.—Pentabromophenol was converted to the ether by treatment with a large excess of allyl bromide as described. Crystallization from petroleum ether (80–100°) gave short colorless needles; m. p. 167–168".

Anal. Subs., 0.2016: 17.96 cc. 0.1 *N* $AgNO_3$. Calcd. for $C_9H_5OBr_5$: Br, 75.61. Found: Br, 75.57.

The β,γ-Dibromo Derivatives.—The above-mentioned compounds were next subjected to the action of excess of bromine as follows. The ether was dissolved in chloroform, finely powdered dried sodium acetate added, the flask placed in an ice-bath and the mixture stirred while there was added gradually slightly more bromine than was required to saturate the side chain and substitute all available positions on the nucleus. The mixture stood for several days, the solvent and excess of bromine were distilled off, water was added to dissolve salts, and the ether extracted with a suitable solvent. The physical constants and analytical data for these products are given in Table III.

TABLE III

PHENYL-β,γ-DIBROMOPROPYL ETHERS

Substituted phenyl	Formula	Crystal form	Yield, %	M. p., °C	Halogen,[d] % Calcd.	Found
2,4-Dichloro-	$C_9H_8OCl_2Br_2$	Oil	95	Distilled at 188 (10 mm.)	63.59	63.3
2,3,4,5-Tetrabromo-	$C_9H_6OBr_6$	Nearly[a] colorless prisms	97	123–124	78.68	78.68
2,6-Dibromo-	$C_9H_8OBr_4$	Colorless needles[b]	96	4849.5	70.77	70.60
Pentabromo-	$C_9H_5OBr_7$	Colorless needles[c]	94	122–123	81.27	81.29

[a] Crystallized from acetic acid. [b] Purified with much difficulty, first by distillation and afterward by repeated crystallization from alcohol. [c] Crystallized from ligroin (80–100°). [d] Brown and Beal, THIS JOURNAL, 45, 1291 (1923).

Action of Alcoholic Potash on the Ethers.—Weighed portions of the β,γ-dibromopropyl ethers were dissolved in hot alcohol, and an alcoholic solution of potassium hydroxide added. After the first vigorous action was over the mixture was refluxed for one hour,[17] the liquid cooled, acidified with nitric acid, and diluted to a measured volume. Duplicate samples of the solution were withdrawn, boiled with measured volumes of standard silver nitrate solution in excess of that required by the bromide ion present and the unchanged silver salt determined by titration. From the values so obtained the weight of bromine removed by alkali in each case was estimated, and the decomposition percentage calculated. The remainder of the acid liquid was extracted with ether, the extract dried with anhydrous sodium sulfate, the solvent distilled off, and the propargyl ether purified in a suitable way. The results are given in the accompanying table.

Salts of the Ethers.—The silver salts were precipitated as nearly colorless solids by mixing alcoholic solution of silver nitrate and the required ether, as directed by Béhal.[18] The cuprous salts were obtained as yellow solids by pouring alcoholic solutions of the ethers into ammoniacal solution of cuprous chloride, while the mercuric salts were prepared as gray precipitates by the use of Nessler's reagent. Analytical data for these compounds are given in Table V.

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[17] When 2,3,4,5-tetrabromophenyl β,γ-dibromo-*n*-propyl ether, described above, was subjected to this treatment, the amount of bromine removed was greater than that corresponding to the loss of two molecular proportions of hydrogen bromide from the side chain, which suggested that some halogen had been lost from the phenyl nucleus, possibly from one of the meta positions. The product was not obtained in the pure form, but it was shown to be an ether, and found to give metallic derivatives.

[18] Béhal, *Ann. chim.*, [6] 15, 423 (1888).

TABLE IV

PHENYL PROPARGYL ETHERS

Substituted phenyl	Formula	Crystal form	Yield, %	M. p., °C.	Halogen,[d,e] % Calcd.	Found
2,4-Dichloro-	$C_9H_6OCl_2$	..............[a]	99	Liq.	35.32	35.14
2,4-Dibromo-	$C_9H_6OBr_2$	Colorless[b] needles	98	65	55.17	55.04
2,6-Dibromo-	$C_9H_6OBr_2$	Colorless" needles	98	58–60	55.17	55.33
2,4,6-Tribromo-	$C_9H_5OBr_3$	Colorless[e] needles	97	136–137	65.04	65.08

[a] Not obtained in crystalline form. Attempts to distil under reduced pressure caused decomposition. [b] Many recrystallizations from dilute alcohol were required for purification. Attempts to distil under partial vacuum caused much decomposition with a distillate passing over at 135" and 10 mm. Contact with air caused the hot material to char instantly. [c] Crystallized from alcohol. [d] Brown and Beal, Ref. d, Table III. [e] Carius method.

TABLE V

SALTS OF PHENYL PROPARGYL ETHERS

Substituted phenyl	Formula	Halogen,[a] % Calcd	Found
2,4-Dichloro-	$C_9H_5OCl_2Ag\cdot AgNO_3$	14.86	14.85
2,4-Dibromo-	$C_9H_5OBr_2Ag\cdot AgNO_3$	28.23	28.02
	$C_9H_5OBr_2Cu$	45.36	45.07
	$C_{18}H_{10}O_2Br_4Hg$	41.13	40.81
2,6-Dibromo-	$C_9H_5OBr_2Ag\cdot AgNO_3$	28.23	28 00
2,4,6-Tribromo-	$C_9H_4OBr_3Ag\cdot AgNO_3$	37.16	37.14
	$C_9H_4OBr_3Cu$	55.61	55.31
	$C_{18}H_8O_2Br_6Hg$	51.28	51.15

[a] Halogen determined by the Carius method.

Summary and Conclusions

1. The hydrogen bromide evolved in the bromination of phenyl alkyl ethers may split them unless sodium acetate is present. The splitting is most complete when the alkyl group is connected through a secondary or tertiary carbon atom.

2. Phenyl allyl ethers containing two or more bromine atoms in the nucleus could not be rearranged by heat.

3. Under most conditions studied in this work the action of bromine on phenyl allyl ether saturates the side chain and substituted two positions in the phenyl radical.

4. The ethers here studied which have bromine in the β,y-positions in the side chain react with alcoholic potash and lose two molecular proportions of hydrogen bromide to give the corresponding propargyl compounds. The latter form cuprous, mercuric and silver salts.

5 Further work is in progress in this Laboratory.

IOWA CITY, IOWA

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CATALYSIS OF POLYMERIZATION BY OZONIDES

BY RAY C. HOUTZ AND HOMER ADKINS

RECEIVED DECEMBER 26, 1930 PUBLISHED MARCH 6, 1931

In view of the important part oxygen apparently plays in the drying of oils, and in the polymerization of various substances such as styrene and isoprene,[1] it seemed worth while to study the action of ozonides in accelerating polymerizations. In addition to the metal halides which are well known as polymerization catalysts, many apparently unrelated materials have been claimed to catalyze the polymerization of dienes, such for example, as alkaline earth alkyls,[2] glycerol, starch, urea,[3] organic peroxides, acid anhydrides, metal oxides and per-salts,[4] and the products obtained by ozonizing isoprene.[5] Since the completion of the experimental work discussed in this paper, Conant and Tongberg[6] have shown that a partially ozonized sample of isoprene polymerized more rapidly at ten to twelve thousand atmospheres' pressure than did unozonized isoprene.

The material used as a catalyst in this investigation was a mixture of the ozonides of two octylenes known as "diisobutylene."[7] It was prepared by passing a mixture of 5% ozone and 95% oxygen into the hydrocarbon at 0–5° without a solvent. The reaction was considered complete when quantitative absorption of the ozone ceased, as shown by the effect of the issuing gas on starch–iodide paper. The product was a viscous, pale yellow oil, having on the average n_D^{25} 1.4425; d_{25}^{25} 0.9707. It was miscible with the common organic solvents and exploded if heated above 50–60°. Upon standing, it decomposed slowly with effervescence, losing its yellow color and explosiveness, decreasing markedly in viscosity, density, and refractive index, and increasing in acidity.

Since the formation of polymers results in an increase in the viscosity of a liquid or solution, viscosity measurements were made in order to compare the rates of polymerization.[8] In general, the method consisted in sealing the samples in test-tubes from which the air had been displaced by a stream of nitrogen. The viscosity of each sample was measured at 25°

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[1] Engler, *8th Int. Congr. Appl. Chem.*, 25, 661 (1912).

[2] Badische Anilin und Soda Fabrik, German Patent 255,786 (Jan. 27, 1912).

[3] Farbenfabriken vom Friedr. Bayer & Co., German Patent 248,399 (March 24, 1911).

[4] Chemische Fabrik Griesheim Elektron, German Patent 281,688 (April 2, 1914); Klatte and Rollet, U. S. Patent 1,241,738 (Oct. 2, 1918).

[5] Badische Anilin und Soda Fabrik, British Patent 22,454 (Oct. 11, 1911); Holt and Steimmig, U. S. Patent 1,189,110 (June 27, 1916).

[6] Conant and Tongberg, THIS JOURNAL, 52, 1659 (1930).

[7] McCubbin and Adkins, *ibid.*, 52, 2547 (1930).

[8] Cf. Stobbe and Posnjak, *Ann.*, 371, 259 (1909).

using an Ostwald viscometer. The tubes were allowed to stand for a time, then broken open and the viscosity redetermined. Each accepted flow-time was the average of four to six trials which checked within 0.1 or 0.2 seconds. Freshly made ozonide was always used in preparing the samples.

TABLE I

CATALYTIC POLYMERIZATION OF STYRENE AND INDENE, EFFECT OF SOLVENT AND TEMPERATURE

Catalyst concn., %	Solution	Temp., °C.	Reaction time	Viscosity Data — Flow time (On sealing)	Viscosity Data — Flow time (On opening)	Viscosity Data — % increase
			Styrene			
None	10% in toluene	100	6 Hrs.	106.6 (a)	106.9	0.3
None	10% in toluene	100	6 Hrs.	106.6 (a)	107.2	0.6
1	10% in toluene	100	6 Hrs.	108.1 (a)	140.1	29.6
1	10% in toluene	100	6 Hrs.	108.1 (a)	139.9	29.4
None	10% in toluene	100	10 Hrs.	106.3 (a)	118.4	11.5
None	10% in toluene	100	10 Hrs.	106.3 (a)	117.6	10.7
1	10% in toluene	100	10 Hrs.	107.7 (a)	150.7	40.0
1	10% in toluene	100	10 Hrs.	107.7 (a)	151.0	40.2
None	10% in toluene	Room	46 Days	43 6 (b)	43.5	−0.2
2	10% in toluene	Room	46 Days	44 5 (b)	47.6	7.0
None	5% in toluene	Room	6 Days	37.3 (c)	37.1	−0.5
None	5% in toluene	Room	6 Days	37.3 (c)	37.2	−0.3
1	5% in toluene	Room	6 Days	37.6 (c)	38.3	1.9
1	5% in toluene	Room	6 Days	37.6 (c)	38.4	2.2
			Indene			
None	No solvent	100	22 Hrs.	111.2 (b)	115.3	3.7
None	No solvent	100	22 Hrs.	111.2 (b)	115.8	4.1
3	No solvent	100	22 Hrs.	114.6 (b)	183.9	60.5
3	No solvent	100	22 Hrs.	114.6 (b)	180.1	57.0
None	10% in toluene	100	22 Hrs.	112.1 (a)	112.5	0.4
None	10% in toluene	100	22 Hrs.	112.1 (a)	112.6	0.5
1	10% in toluene	100	22 Hrs.	113.7 (a)	115.6	1.7
1	10% in toluene	100	22 Hrs.	113.7 (a)	115.0	1.1

The flow time for water of viscometer (a) was 149.4 sec., for (b) 59.3 sec. and for *(c)* 50.6 sec.

Polymerization of Styrene.[9]—Preliminary experiments showed that a small concentration of the ozonide caused styrene to polymerize rapidly, the mixture becoming almost solid in the course of a week. A study was then made of the effect of catalyst concentration on the rate of polymerization. Solutions containing from 0 to 4% ozonide in styrene were placed in a thermostat at 25°. The rates of viscosity increase of styrene using various amounts of catalyst are shown in Fig. 1. The viscometer first used has a water-flow time of **59.3** seconds, but as the viscosities increased the flow times became too large to be convenient, so another having a much shorter *flow* time was employed. The flow times shown in Fig. 1 are all

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[9] Cf. Staudinger and Heuer, *Ber.*, **63,** 222 (1930).

calculated to the first viscometer on the basis of the flow times of sulfuric acid through the two viscometers. The data in Fig. 1 show that increased concentration of ozonide up to 2% was very effective in increasing the rate of polymerization but that increasing the concentration of catalyst beyond this amount had little effect. The 0.5% curve seems to indicate that an induction period was necessary, since nearly two hundred hours elapsed before a rapid viscosity increase began. Stobbe and Posnjak[8] found that styrene which had stood for fourteen days was polymerized more rapidly bv heat and light than freshly distilled styrene. Probably styrene becomes activated toward polymerization upon standing.

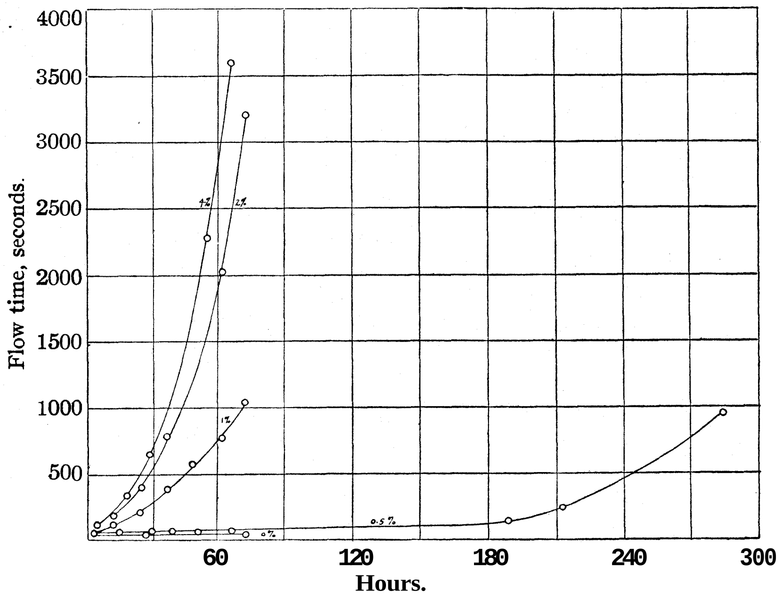

Fig. 1.—Relation of concentration of ozonide to rate of polymerization of styrene. The viscosities at 25° of four samples of styrene containing 0.5, 1, 2 and 4%, respectively, of diisobutylene ozonide are plotted against the time in hours elapsing after the addition of the latter to the styrene.

To determine whether the catalyst was active at elevated temperatures, tubes containing 0, 1 and 4% ozonide were sealed and placed in a steam jacket (nearly 100°) for thirty minutes. The contents of the tubes containing 1 and 4% ozonide had become almost solid. The styrene in the tubes containing no ozonide had thickened considerably, but less than those into which the catalyst had been introduced. The polymerization of styrene was also studied in toluene solution, at both room temperature and 100°. An abstract of the data is given in Table I. The changes in viscosity show that the catalyst was active toward styrene in toluene solution, at both temperatures.

Polymerization of **2,3-Dimethylbutadiene-1,3.**—Solutions containing from 0 to 4% ozonide in freshly distilled dimethylbutadiene were made and left in sealed tubes at room temperatures for forty-four days. The viscosity increases noted were as follows: for 0% ozonide, 63.5, 67.5%; 0.125% ozonide, 83.0, 81.0%; 0.25% ozonide, 93.5, 90.5%; 0.5% ozonide, 100, 99%; 1.0% ozonide, 118, 114%; 2.0% ozonide, 114, 111%; 4.0% ozonide, 117, 122%. It is apparent that the catalytic power of the ozonide toward the diene increased with increasing concentration, but that increments became decreasingly effective, just as was found in the case of styrene.

Polymerization of **"Methylpentadiene."**—Tubes were sealed containing 0.0 and 3.0% of ozonide in methylpentadiene, and allowed to stand for ninety days at room temperature. The increases in viscosity were as follows: 0% catalyst, 1.2% increase; 3% catalyst, 10.4% increase. This result was confirmed by the fact that there was much more of the sticky, rubber-like polymer left on evaporation of the sample containing 3% ozonide than there was from the sample containing no ozonide.

Polymerization of **Indene.**—Samples were sealed and allowed to stand for thirty days. After measuring viscosity they were resealed and left for one hundred and twenty days longer. The percentage increases in viscosity during thirty days were as follows: 0% ozonide, 0.3, 0.7%; 2% ozonide, 12.9, 14.0%; at the end of one hundred and fifty days, 0% ozonide. 3.0, 2.7%; 2% ozonide, 50.5, 56%. The data in Table I show that the ozonide is catalytically active toward indene at 100° as well as at room temperature, and also in toluene solution.

Polymerization of **Furfuryl Alcohol.**—Since furfuryl alcohol turns dark with the formation of resinous products on contact with air, the effect of the ozonide on this substance was studied both in air and in nitrogen. Tubes were sealed and allowed to stand at room temperature for forty days. In the tubes containing nitrogen, the viscosity increases were as follows: 0% catalyst, 1.0, 2.1%; 2% catalyst, 45.6, 47.2%. In the tubes containing air: 0% catalyst, 21.6%; 2% catalyst, 62.4, 66.4%. The percentage of increase in the tubes containing both catalyst and air is approximately the sum of the separate effects of catalyst and air. Since the ozonide liberates some oxygen as it decomposes on standing, the polymerizing effect may be due merely to the presence of the liberated molecular oxygen.

Attempted Polymerization of Other Compounds.—Solutions containing 2% ozonide in trimethylethylene and diisobutylene were sealed and allowed to stand for three to four months. No significant viscosity change had occurred during that time. Stilbene and saligenin were studied similarly in solution using dibutyl ether, dioxane, and toluene as solvents. When no significant viscosity change occurred in three months at ordinary temperatures, higher temperatures were employed (60 and 100°). Viscosity changes in all cases were too small to be significant.

Deterioration of Catalyst.—A sample of ozonide which had stood for several months was found to be active toward styrene. If the ozonide itself is concerned with the catalytic effect, fresh samples should be more active than old ones. If, on the contrary, decomposition products are more active, the catalytic power should increase somewhat on standing. To test this point, the catalytic power of the ozonide was measured on five successive days and again after an interval of twelve days, by noting the viscosity increase produced in freshly distilled styrene samples in twenty-four hours. Each day a fresh solution of the ozonide in styrene was made, and the viscosity increase produced in twenty-four hours noted. Both ozonide and solutions were kept in a thermostat at 25°. The results are plotted in Fig. 2. The decrease in viscosity of the ozonide was very rapid for about three days and during this time the catalytic power decreased rapidly. If decrease in viscosity may be taken as a measure of the decomposition of the ozonide, the latter parallels the decrease in catalytic power, indicating that the ozonide itself, rather than decomposition products, is concerned with the catalysis of polymerization. If ozonization of diisobutylene is stopped just at the point at which quantitative absorption ceases, the ozonide has a very high viscosity. If stopped before this point is reached, the product is much less viscous, due, no doubt, to the presence of diisobutylene. If ozonization is carried beyond this point, the product is also less viscous. This may be due to the formation of perozonides and oxidation products, as indicated by the work of Brus and Peyresblancques.[10]

Preparation of Reagents.—Diisobutylene was prepared as by Edgar.[11] Styrene was prepared as by Abbot and Johnson.[12] 2,3-Dimethylbutadiene-1,3 was prepared from pinacol in 60% yield.[13] Stilbene was prepared essentially according to the method of Hell.[14] Saligenin (*o*-hydroxybenzyl alcohol, m. p. 84°) was obtained by hydrogenation of salicylaldehyde over nickel.[15] The aldehyde (56 g.) was prepared from 250 g. of phenol by the method of Reimer and Tieman.[16] Trimethylethylene (34–38°) was obtained from tertiary amyl alcohol.[17] Methylpentadiene was prepared by the dehydration of 2-methylpentadiol-2,4. The latter was obtained by the reduction of diacetone alcohol. Eighty-three grams of the diol were dehydrated using 1.4 g. of aniline

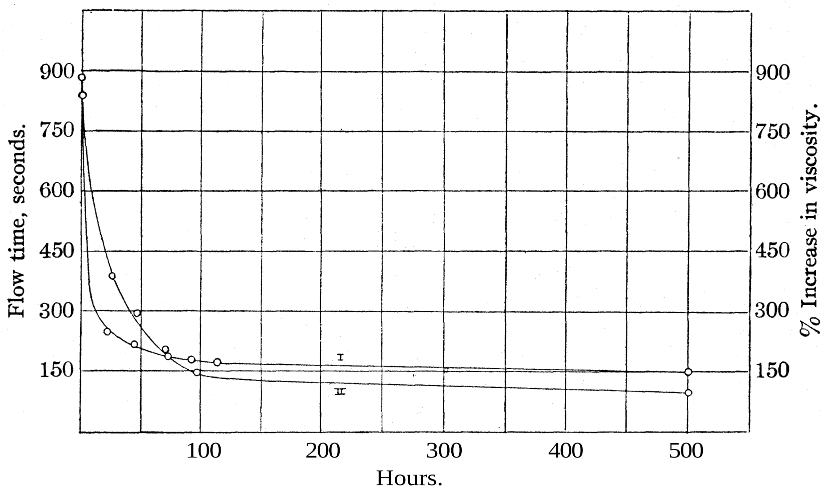

Fig. 2.—Relation of age to catalytic activity of ozonide. In curve I the viscosity of diisobutylene ozonide (expressed in flow time in seconds) is plotted against the time in hours that had elapsed after its preparation. In curve II there is plotted the percentage increase in the viscosity after twenty-four hours at 25° of a sample of styrene containing 2% of ozonide, against the hours that had elapsed between the preparation of the ozonide and its addition to the sample of styrene.

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[10] Brus and Peyresblancques, *Compt. rend.*, 190,685 (1930).

[11] Edgar, *Ind. Eng. Chem.*, 19, 145 (1927).

[12] Abbot and Johnson, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII. p. 84.

[13] Kyriakides, THIS JOURNAL, 36, 992 (1914).

[14] Hell, *Ber.*, 37, **453** (1904).

[15] Adkins and Cramer, THIS JOURNAL, 52, 4354 (1930).

[16] Reimer and Tieman, *Ber.*, 9, 824 (1876).

[17] Earl, *J. Proc. Roy. Soc. N. S. Wales*, 61, 68 (1927).

hydrobromide as a catalyst as in the preparation of 2,3-dimethylbutadiene-1,3. The oil layer was found to boil at 72–128°. The formation of some of a methylpentenol was indicated by the fact that the weight of the water layer was low as well as by the boiling range of the product. An attempt to complete the dehydration with oxalic acid resulted in the formation of dark, high-boiling products. About 15 g. of olefin boiling at 74–76° was collected as a mixture of two possible methylpentadienes.

Summary

A mixture of the ozonides of two octylenes has been found to catalyze the polymerization of styrene, indene, 2,3-dimethylbutadiene-1,3, a methylpentadiene, and furfuryl alcohol. It has been found to be inactive as a polymerization catalyst toward stilbene, o-hydroxybenzyl alcohol, trimethylethylene, and the mixture of octylenes from which it is made. The catalyst was active at room temperature and 100° and in a solution in toluene. The ozonide underwent a change on standing especially during the first two days after its preparation and lost a large part of its catalytic power.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

CHARACTERIZATION OF ALKYL HALIDES AND ORGANOMAGNESIUM HALIDES[1]

BY A. M. SCHWARTZ AND JOHN R. JOHNSON

RECEIVED DECEMBER 26, 1930 PUBLISHED MARCH 6, 1931

Since organomagnesium halides react smoothly with aryl isocyanates to produce substituted amides that are usually crystalline solids, this reaction is suitable for the identification of organomagnesium halides and of halides that can be converted into these. Gilman and his collaborators[2] have used phenyl and α-naphthyl isocyanates for this purpose and have pointed out that a-naphthyl isocyanate enjoys some advantages over phenyl isocyanate. The most important of these appears to be the fact that the resulting a-naphthyl amides can be purified more readily than the anilides. This disadvantage attending the use of phenyl isocyanate can be minimized by avoiding an excess of the isocyanate and is more than counterbalanced, in our experience, by the fact that only a small number of the a-naphthyl amides are described in the literature. Of the ten α-naphthyl amides prepared by Gilman and Furry, five had not previously been reported. On the other hand, the anilides of all of these

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[1] A paper presented at the St. Louis Meeting of the American Chemical Society, April 18, 1928. The present report contains additional data not included in the preliminary paper.

[2] Gilman and Furry, THIS JOURNAL, 50, 1214 (1928). This article gives an excellent review of previous work dealing with the action of aryl isocyanates on organometallic halides.

acids have been described in the literature. For purposes of identification, with a minimum preparation of new compounds, it appears preferable to use phenyl isocyanate.

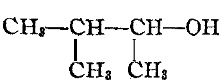
In the present study the alcohols were used as the principal starting materials, since the method lends itself to the characterization of certain secondary and tertiary alcohols and alkyl halides that cannot be identified by the usual methods. All of the isomeric propyl, butyl and amyl alcohols were carried through the series of reactions indicated below

$$R{-}OH \xrightarrow[PX_3]{HX} R{-}X \xrightarrow[\text{ether}]{Mg} R{-}MgX \xrightarrow[H_2O]{C_6H_5NCO} R{-}CO{-}NH{-}C_6H_5$$

In addition to this complete series of alcohols, several other alcohols and alkyl halides were examined. The details of these preparations are shown in Table I. In practice, this method is limited principally by the yield in the conversion of the halide into the organomagnesium halide.

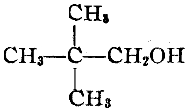
In general, the anilides proved to be satisfactory derivatives for identification, but in several instances the melting points of isomeric compounds differ by only a few degrees. In these cases it is necessary to prepare authentic specimens of known anilides and to use mixed melting point determinations to establish the identity of the unknown anilide. Tests of the mixed melting point procedure showed that unlike anilides of approximately the same melting point gave a marked depression of the melting point when mixed together.

Two of the isomeric amyl alcohols, 3-methylbutanol-2 (I) and 2,2-dimethylpropanol-1 (II) suffered an intramolecular rearrangement in the course of the above series of reactions. Both of these alcohols gave the anilide of dimethylethylacetic acid (111), identical with that obtained from *tert.*-amyl alcohol



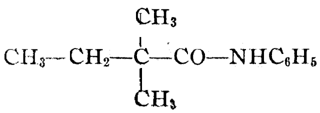
$$CH_3{-}\underset{CH_3}{CH}{-}\underset{CH_3}{CH}{-}OH$$

I



$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2OH$$

II



$$CH_3{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CO{-}NHC_6H_5$$

III

It is probable that this rearrangement occurred in the conversion of the alcohols into the corresponding chlorides since the chlorides agree in physical properties with *tert.*-amyl chloride. Although several special methods were used in the preparation of the chlorides, such as the action of thionyl chloride in the presence of pyridine,[3] we did not obtain any anilide other than that of dimethylethylacetic acid.

In the case of allylmagnesium bromide[4] the resulting anilide was an

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[3] Darzens, *Compt. rend.*, **152, 1314 (1011); Kirner, THIS JOURNAL, 50, 3958** (1928).

[4] Gilman and McGlumphy, ***Bull.** soc. chim.*, [4] 43, 1322 (1928).

oil that could not be crystallized or distilled. On warming with very dilute sulfuric acid the oil was converted to a solid, from which crotonic anilide was isolated by repeated crystallizations. In this case the original anilide was probably impure vinylacetic anilide, and the subsequent treatment effected a rearrangement to form the more stable compound in which the double bond is conjugated with the carbonyl group

$$CH_2{=}CH{-}CH_2{-}MgBr \xrightarrow{C_6H_5NCO} CH_2{=}CH{-}CH_2{-}CO{-}NHC_6H_5 \longrightarrow CH_3{-}CH{=}CH{-}CO{-}NHC_6H_5$$

It seemed of interest to investigate the behavior of an optically active alkyl halide, in which the halogen is directly attached to the asymmetric

TABLE I

EXPERIMENTAL DATA

Alcohol	Halide of RX	Yield[a] of RMgX, %	Anilide of acid	M. p., °C. (corr.)
n-Propyl	Br	84	*n*-Butyric	92
Isopropyl	Br	82	Isobutyric	103
n-Butyl	Br	78	*n*-Valeric	63
Isobutyl	Br	81	Isovaleric	109.5
Sec.-butyl	Br	63	Methylethylacetic	108
Tert.-butyl	Cl	47	Trimethylacetic	128
n-Amyl	Br	76	n-Caproic	96
Isoamyl	Br	86	Isocaproic	108.5
Pentanol-2	Br	79	Methyl-*n*-propylacetic[b]	88
Pentanol-3	Br	88	Diethylacetic"	123–124
2-Methylbutanol-1	Br	66	*Sec.*-butylacetic	88
3-Methylbutanol-2	Cl	17	*Dimethylethylacetic*[d]	92
2,2-Dimethylpropanol	Cl	15	*Dimethylethylacetic*[d]	92
Tert.-amyl	Cl	38	Dimethylethylacetic	92
n-Hexyl	Br	85	n-Heptoic	69
n-Heptyl	Br	86	n-Octoic	57
dl-Octanol-2	Br	63	dl-2-Methyloctoic	72–73
d-Octanol-2	Br	61	dl-2-Methyloctoic	72–73
Cyclohexanol	Br	78	Hexahydrobenzoic	146
Benzyl	Cl	92	Phenylacetic[b]	117
Allyl	Br	62	*Crotonic*[c,d]	113–114

[a] The yields of RMgX are significant because the application of this method of identification is limited in practice by the successful transformation of the halide into RMgX. The yields tabulated here are merely those of typical preparations under ordinary conditions and are not usually the highest that have been attained. Data on the yields of RMgX from a variety of halides, using a standardized procedure, are found in papers by Gilman and his collaborators [THIS JOURNAL, 45, 2462 (1923); 51, 1576 (1929)].

[b] For comparison and checking, this anilide was also prepared from a pure specimen of the corresponding acid obtained by an independent synthesis

[c] The purification of this anilide was difficult and involved an unusually great loss of material.

[d] The structure of this anilide does not correspond to that of the original alcohol; an intramolecular rearrangement occurred in this series of reactions.

carbon atom. For this purpose d-2-bromooctane was chosen, and the resulting anilide was compared with that obtained from dl-2-bromooctane. The optically active halide was found to give a completely inactive anilide, dl-2-methyloctanoic anilide, identical in all respects with that obtained from the racemic halide.[5]

Experimental

Alcohols.—*n*-Propyl, isopropyl and n-butyl alcohols were obtained by fractional distillation of commercial products of high purity. With these exceptions all of the alcohols were prepared synthetically by the conventional methods (usually by Grignard syntheses) and were carefully purified. In a number of supplemental experiments we used specimens of various isomeric amyl alcohols furnished by the Sharples Solvents Corporation, who kindly supplied us with generous samples of these materials.

Alkyl Halides.—The primary and secondary alcohols were usually converted to the bromides, since the primary and secondary alkyl bromides react with magnesium more readily than the chlorides and give higher yields than the iodides. In supplementary trials on a small scale, several chlorides and iodides were used. The tertiary alcohols (and a few of the more reactive primary and secondary alcohols) were converted to the chlorides.

The straight-chain primary bromides were prepared by refluxing the alcohols with a solution of hydrobromic and sulfuric acids obtained by passing sulfur dioxide into a mixture of bromine and ice,[6] without any additional sulfuric acid. The branched chain and secondary bromides were prepared by refluxing the alcohols with 48% aqueous hydrobromic acid without the addition of sulfuric acid. Addition of the latter may lead to the production of isomeric bromides in some cases, and it is extremely difficult to separate these by fractional distillation The tertiary alcohols were converted to the chlorides by shaking with concd. hydrochloric acid? Octanol-2 and cyclohexanol were converted to the bromides by the use of phosphorus tribromide.

Organomagnesium Halides.—The Grignard reagents were prepared according to the conventional methods; a sufficient quantity of ether was used so that the resulting solutions contained from 0.5 to 1.0 mole of RMgX per liter. After standing for at least twelve hours, the solutions were decanted through a plug of glass wool and titrated with standard acid to determine the yields.[8]

Reaction with Phenyl Isocyanate.—A solution of slightly less than the theoretical amount (usually 0.90 mole) of phenyl isocyanate, dissolved in ten volumes of ether, was added dropwise to a solution of the organomagnesium halide, with shaking. It is important to avoid any hydrolysis of the isocyanate and to insure a complete reaction, in order to obtain a pure anilide. The reaction mixture was allowed to stand with occasional shaking for an hour (except for very small runs, which could be hydrolyzed after a few minutes). Hydrolysis was effected by adding, cautiously, cold water containing a little hydrochloric acid. It is necessary to shake the resulting mixture thoroughly in order to obtain a complete hydrolysis of the magnesium derivative of the anilide. The

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[5] We have not yet determined whether the racemization occurs in the formation of the Grignard reagent or in the reaction of the latter with phenyl isocyanate. From theoretical considerations it appears more likely that racemization occurs in the formation of the Grignard reagent from the secondary alkyl halide.

[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 5.

[7] *Ibid.*, Vol. VIII, 1928, p. 50.

[8] Gilman, Wilkinson, Fishel and Myers, THIS JOURNAL, 45, 150 (1923).

ether layer was separated[9] and dried with magnesium sulfate; the crude anilide remained after distilling off the solvent. The anilides were usually crystallized from ethyl ether, petroleum ether, or methyl alcohol. It is most satisfactory to effect purification by crystallization from two different solvents; the best results were obtained by a crystallization from petroleum ether followed by ethyl ether. Methyl alcohol can be used for anilides that do not respond to purification by these solvents. The resulting anilides are white crystalline solids with sharp melting points. In a few cases it was necessary to use decolorizing charcoal to obtain colorless products. The yields of the crude anilides were usually from 80–90% of the theoretical quantity, based upon the phenyi isocyanate. The losses in subsequent purification varied from 10–50%.

Procedure for Identification of Alkyl Halides.—In a dry test-tube, provided with a *cork* bearing a calcium chloride tube, is placed 0.4 g. (17 milliatoms) of magnesium turnings. A small crystal of iodine is added and the tube is heated gently until the iodine has reacted completely. The tube is allowed to cool and a solution of 1–2 g. (approximately 10 millimoles) of the dry alkyl halide in 4–5 cc. of dry ether is added. With many halides the reaction starts vigorously and it is necessary to cool the tube in a bath of cold water. In these cases it is preferable to add slowly the solution of the alkyl halide to the magnesium. If the reaction does not start spontaneously, the tube is heated gently by immersion in a beaker of warm water. After the reaction has started[10] the ether is maintained in gentle ebullition until the alkyl halide has reacted completely. After cooling, about 10 cc. of dry ether is added and the unreacted magnesium is allowed to settle. The solution is decanted quickly into another dry test-tube of large capacity, and 4–5 cc. of a 10% ethereal solution of phenyl isocyanate (3–4 millimoles) is added dropwise, with shaking. The tube is protected from atmospheric moisture and allowed to stand for a few minutes with intermittent shaking. The reaction mixture is poured *cautiously* into 20 cc. of ice water containing 1 cc. of concd. hydrochloric acid, and the mixture is agitated thoroughly. The ether layer is separated,[9] dried over anhydrous magnesium sulfate and evaporated. The residual crude anilide is crystallized from appropriate solvents, and if necessary decolorized by the addition of a little decolorizing carbon.

Summary

1. The conversion of a series of alcohols into the corresponding alkyl halides and organomagnesium halides has been investigated.

2. It has been found satisfactory to characterize these organomagnesium halides by reaction with phenyl isocyanate. The resulting anilides are crystalline solids that are suitable for identification purposes.

3. The application of this method to certain branched chain alcohols is limited by the fact that intramolecular rearrangements may lead to anilides that do not correspond in structure to the original alcohol.

4. An optically active halide, d-2-bromooctane (in which the halogen

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[9] With anilides that are very slightly soluble in ether, a portion of the product separates as a crystalline precipitate and remains suspended at the interface. This portion was removed by filtration, dried and combined with the fraction obtained from the ether layer.

[10] In working with small quantities, difficulty is sometimes experienced in starting the reaction. In refractory cases, the reaction can often be initiated by the addition of a small quantity of Gilman's magnesium--copper alloy, that has been activated by heating with an equal weight of iodine.

is directly attached to the asymmetric carbon atom) led to a completely inactive anilide.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

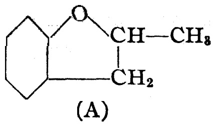
PROPARGYL ETHERS OF PHENOL

BY CHARLES D. HURD AND FRANK L. COHEN

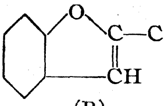
RECEIVED DECEMBER 29, 1930 PUBLISHED MARCH 6, 1931

In contrast to the considerable information concerning the pyrolysis of allyl aryl ethers,[1] little is known concerning the propargyl aryl ethers. Whereas the former tpye changes on refluxing into o-allylphenols, the latter has been reported[2] to yield nothing but nondescript resins. Thus only tars were found when phenyl propargyl ether or p-bromophenyl propargyl ether was refluxed alone or refluxed in diamyl ether.

For the rearrangement of the propargyl ethers to follow the course of the allyl ethers, the anticipated product would be o-hydroxyphenylallene, rather than o-propargylphenol. It appears to be the gamma carbon of the unsaturated chain which becomes attached to the aromatic nucleus during the rearrangement. Thus, just as $C_6H_5OCH_2CH{=}C^*H_2$ rearranges into ortho $HOC_6H_4C^*H_2CH{=}CH_2$, so it might be anticipated that C_6H_5O-$CH_2C{\equiv}C^*H$ would change into ortho $HOC_6H_4C^*H{=}C{=}CH_2$. Furthermore, since 2-methylcoumaran, (A) is a by-product from the pyrolysis of the allyl ether, it might be anticipated, that 2-methylcoumaron, (B), would result from the propargyl ether. Both hydroxyphenylallene and methylcoumaron are structures which might be expected to polymerize readily. It is conceivable that either or both of these substances were the precursors of the tar which was noticed from the pyrolysis of propargyl phenyl ether.



(A)

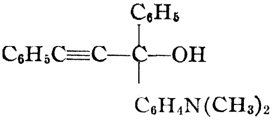


(B)

In extending this subject we endeavored to synthesize the phenyl ethers of the following propargyl alcohols and to study their pyrolysis:

Triphenylpropargylalcohol	$C_6H_5C{\equiv}C{-}C(C_6H_5)_2OH$
Trimethylpropargyl alcohol	$CH_3C{\equiv}C{-}C(CH_3)_2OH$
γ-Methylpropargyl alcohol	$CH_3C{\equiv}C{-}CH_2OH$
1-Phenylethinylcyclohexanol-1	$C_6H_5C{\equiv}C{-}C(CH_2)_5OH$

α,γ-Diphenyl-α-*p*-dimethylaminophenylpropargyl alcohol



$$C_6H_5C{\equiv}C{-}\underset{C_6H_4N(CH_3)_2}{\overset{C_6H_5}{C}}{-}OH$$

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[1] This topic is summarized in Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, 1929, pp. 214–228.

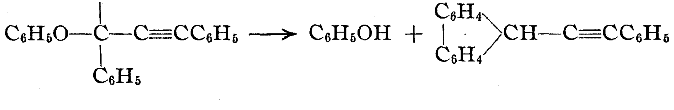
[2] Powell and Adams, THIS JOURNAL, 42, 654 (1920).

Of these compounds, only the first and third appear to have been described previously.

The first three of these alcohols were converted into the chlorides by phosphorus trichloride. The fourth reacted with phosphorus pentachloride but the reaction product did not analyze correctly for the desired halide. This reaction is being studied further. All attempts to convert the fifth alcohol into its chloride were unsuccessful. Dry hydrogen chloride, concd. or dilute hydrochloric acid, and phosphorus tri- and pentachlorides were all tried with variations in temperature and concentration. It seemed, however, that even small amounts of acid were sufficient to give rise to tarry materials from which nothing could be isolated, not even the original alcohol. In the absence of evidence to the contrary, it has been assumed that the propargyl chlorides, $R-C\equiv C-CR_2Cl$, did not rearrange[3] into the chloroallenes, $RCCl=C=CR_2$

Synthesis of the Phenyl Ethers.—With trimethylpropargyl chloride and with y-methylpropargyl chloride it was possible to synthesize the respective phenyl ethers by heating in acetone solution with phenol and potassium carbonate. This is analogous to the method which is commonly used in making the allyl ethers. In contrast to this, it was necessary to use sodium phenoxide to effect reaction with triphenylpropargyl chloride. Even more resistant was the material which was considered (temporarily, at least) to be 1-phenylethinylcyclohexyl chloride. In fact, no satisfactory reaction with phenol or sodium phenoxide could be achieved in spite of several modifications of conditions.

Pyrolysis of the Ethers.—All three of the ethers were found to decompose on heating, but none was found to pyrolyze into an ortho substituted phenol. In fact, distinct differences of reaction mechanism were apparent in all three cases. Triphenylpropargyl phenyl ether was the most resistant to heat, but at 300° it pyrolyzed into phenol and 9-phenylethinylfluorene



$$C_6H_5O-\underset{C_6H_5}{\overset{C_6H_5}{C}}-C\equiv CC_6H_5 \longrightarrow C_6H_5OH + \begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!\!>CH-C\equiv CC_6H_5$$

The yield was about 45%. This reaction is similar evidently to the pyrolysis of triphenylmethyl chloride,[4] wherein hydrogen chloride was detached at temperatures above 200° and 9-phenylfluorene formed. Similar also is the production of phenyl-a-naphthofluorene by refluxing diphenyl-a-naphthylchloromethane[5] with zinc chloride in acetic acid.

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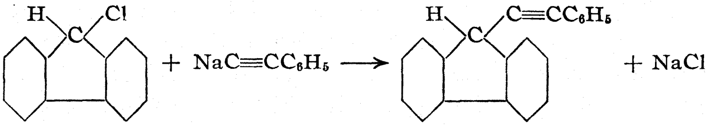
[3] See Willemart, *Compt. rend.*, 187, 385 (1928); 188, 1172 (1929).

[4] Hemilian, *Ber.*, 7, 1208 (1874); 11, 202, 837 (1878); E. and O. Fischer, *Ann.*, 194, 257 (1878); Schwarz, *Ber.*, 14, 1522 (1881); Nef, *Ann.*, 309, 167 (1899).

[5] Ullmann and Mourawiew-Winigradoff, *Ber.*, 38, 2213 (1905).

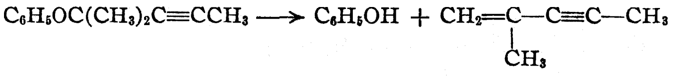
Although it is easy to picture the production of 9-phenylethinylfluorene and 9-phenylfluorene from triphenylpropargyl phenyl ether and triphenylmethyl chloride, respectively, no ready explanation suggests itself as to why other triphenylpropargyl derivatives such as the chloride[6] or acetate[7] fail to undergo a similar type of pyrolysis and yield 9-phenylethinylfluorene. Instead, these substances give rubrene, $C_{42}H_{28}$ (m. p. 331'). An intermediate compound, $C_{42}H_{29}Cl$, which is capable of quantitative conversion into rubrene, is isolable from the chloride by careful heating, but no mention has been made of phenylethinylfluorene. Robin reported that traces only of rubrene were obtained on heating triphenylpropargyl benzoate or triphenylpropargyl methyl ether, but that fair amounts of a yellow hydrocarbon of m. p. 245" were isolated from these substances. We found no rubrene in the pyrolytic products of triphenylpropargyl phenyl ether, but we did isolate traces of a solid melting between 240–250°, which was presumably the same as Robin's compound.

To prove the structure of 9-phenylethinylfluorene, its synthesis was effected from fluorene through fluorenone, 9-hydroxyfluorene and 9-chlorofluorene. This last was condensed with sodium phenylacetylide



The 9-phenylethinylfluorene thus synthesized was identical with the product of the pyrolysis.

Turning now to trimethylpropargyl phenyl ether, it was found to be much more susceptible to heat. Its temperature of decomposition was 160°, as compared to 300° which was required for the triphenylpropargyl phenyl ether. Tar formation was marked, but there was an appreciable yield of phenol and methyl-2-pentene-1-ine-3, in accordance with the equation



$$C_6H_5OC(CH_3)_2C{\equiv}CCH_3 \longrightarrow C_6H_5OH + CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}C{\equiv}C{-}CH_3$$

The ene–ine compound, C_6H_8, was also isolated as a by-product in the synthesis of trimethylpropargyl alcohol and of trimethylpropargyl chloride. Depending on the temperature used, yields of the ene–ine from the alcohol reached as high as 60%. No doubt higher yields could be obtained with facility. This hydrocarbon, b. p. 75–77°, represents an extremely interesting type inasmuch as it possesses conjugation of the rare ene–ine type rather than of the common diene type. Its conjugation was attested to by

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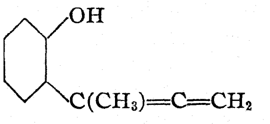
[6] **Moureu, Dufraisse and Dean, *Compt. rend.*, 182, 1440 (1926); Moureu, Dufraisse and Robin, *ibid.*, 188, 1582 (1929).**

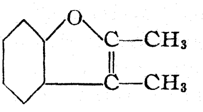
[7] **Robin. *ibid.*, 189, 337 (1929).**

the fact that sodium caused it to polymerize to a black, rubber-like substance in the course of a few hours.

The pyrolysis of γ-methylpropargyl phenyl ether was necessarily different from the other ethers since it possessed no α-phenyl group to give rise to fluorene formation and no α-methyl group to yield a conjugate eneine. Phenol was detected as a reaction product, but only in traces. No gas was evolved. Instead, the chief reaction product was a tar, possessing a molecular weight of about 400. Since the molecular weight of the original ether, or of its isomers such as



or



is 146, this suggests a trimer (mol. wt. 438) as the major component of the tarry mixture. In this polymerization process, most of the original unsaturation was consumed since bromine (in chloroform solution) was absorbed only in trivial amounts. Whether or not the tar was produced as the result of prior allene formation cannot be stated, but if such was the case it is fairly certain that none of the allene escaped the polymerization process.

Experimental Part

Phenylacetylene.—This was prepared by the method of "Organic Syntheses," Vol. VI. An alteration, noted in Volume VIII, p. 124, was the use of potassium hydroxide (2 parts) and sodium hydroxide (1 part) for the fused alkali rather than the former alone. The phenylacetylene was carefully fractionated and the fraction boiling at 140–141° (750 mm.) used. For the work described below, this was an essential step. The material was converted into sodium phenylacetylide by Nef's[8] method. In our use of this salt, it was not removed from the ether wherein it was made.

Phenylethinyl Phenyl Ketone.—Nef's directions[9] were followed for the synthesis of this ketone from sodium phenylacetylide and benzoyl chloride. After purification by vacuum distillation, for a time the ketone resisted solidification. Finally, a solid, m. p. 53–55°, was obtained in 74% yield. Nef's value was 49–50°. André,[10] who prepared this ketone from benzoyl bromide and sodium phenylacetylide, also reported a melting point of 49°. That the value is higher than any of these, namely 65–66°, is shown below.

To effect another synthesis of this ketone, the following reactions were developed

$$C_6H_5C{\equiv}C{-}COCl + C_2H_5OH \longrightarrow C_6H_5C{\equiv}C{-}CO_2C_2H_5 + HCl$$

$$C_6H_5C{\equiv}C{-}CO_2C_2H_5 + C_6H_5MgBr \longrightarrow C_6H_5C{\equiv}C{-}CO{-}C_6H_5 + C_2H_5OMgBr$$

Ethyl cinnamate was converted into phenylpropiolic acid by Perkin's[11] method and this acid changed into the acid chloride in 74% yield by thionyl chloride.[12] We found that

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[8] Nef, *Ann.*, 308, 275 (1899).

[9] Ref. 8, p. 276.

[10] André, *Ann. chim.*, [8] 29, 562 (1913).

[11] Perkin, *J. Chem. Soc.*, 45, 172 (1884).

[12] Watson, ibid., 85, 1324 (1904); Ruhemann and Merriman, *ibid.*, 87, 1389 (1905).

direct esterification of propiolic acid with ethanol and hydrogen chloride (Perkin's method) was impractical because of low yields (33%). Double this yield was obtained from the acid chloride.

Ethyl **Phenylpropiolate.**—A solution of phenylpropiolyl chloride (39 g.) in absolute alcohol (80 cc.) was refluxed for four hours. Then the solution was poured into water and an oil separated. This was extracted with ether, washed with dilute sodium carbonate solution, then with water, dried, and fractionally vacuum-distilled. The yield of the ester was 28.4 g., which is 65% of the theoretical.

Phenylethinyl Phenyl Ketone.—A solution of 0.15 mole of phenylmagnesium bromide in 150 cc. of dry ether was prepared. To this, 10 g. of ethyl phenylpropiolate (0.057 mole) in 100 cc. of dry ether was added slowly. After standing for two hours, the solution was poured into cold, dilute sulfuric acid for hydrolysis. The ether layer was separated and allowed to evaporate at room temperature. A very thick oil was obtained. It failed to crystallize by itself in the cold after two days, but the addition of a little petroleum ether to the surface of the oil caused it to set to a solid mass of very fine crystals. These were filtered off and washed with a small amount of petroleum ether. When dry, the crystals of phenylethinyl phenyl ketone weighed 10 g.; this is an 85% yield. These crystals melted at 43–54" and after several recrystallizations from alcohol the melting point was raised to 65–66°. The boiling point at 15 mm. was found to be 200–202°. This confirms André, who reported 200–205° at 14 mm. Inasmuch as the melting point differed from the older value, the pure material was analyzed.

Anal. Subs., 0.1415: CO_2, 0.4513; H_2O, 0.0621. Calcd. for $C_{15}H_{10}O$: *C*, 87.4; H, 4.89. Found: C, 87.0; H, 4.87.

Although the yields in this synthesis were quite satisfactory, Nef's method involves the use of simpler intermediates and is to be preferred for that reason. It is interesting to note that Wilson and Hyslop[13] synthesized triphenylpropargyl alcohol, rather than phenylethinyl phenyl ketone, by the interaction of ethyl phenylpropiolate and phenylmagnesium bromide. In their procedure, the reaction mixture was kept in a freezing solution of ice and salt during the mixing and the duration of the experiment was "overnight" instead of two hours. Otherwise their steps were very similar to ours.

Synthesis of **Triphenylpropargyl** Alcohol.—In addition to Wilson and Hyslop's method, three other plans have been recorded for the synthesis of this alcohol. (1) Phenylethinyl phenyl ketone[14] plus phenylmagnesium bromide, with a reported yield of "excellcnt." (2) Benzophenone[15] plus phenylethinylmagnesium bromide, in 79% yield. (3) Benzophenone[16] plus sodium phenylacetylide. Nef's yield in this reaction was 54%.

After using all of these methods we reached a preference for the last. However, with Nef's directions very poor yields (0–10%) were obtained. The trouble seemed to be largely in the purification process. It was found that crystallization was a poor method for removing the impurities so, in order to minimize them, the reacting materials were carefully purified before use. Under these conditions the reaction mixture was almost colorless and subsequent crystallization and purification without distillation of unreacted materials was possible. The yields were increased to 65–70% of the theoretical.

To a mixture of 0.1 mole of freshly prepared sodium phenylacetylide in 100 cc. of

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[13] Wilson and Hyslop, J. *Chem. Soc.*, **123,** 2612 (1923).

[14] Kohler, Am. *Chem. J.*, 38, 561 (1907).

[15] Hess and Weltzien, ***Ber.***, 54, 2518 (1921).

[16] Nef, **Ann.**, **308,** 282 (1899); Moureu, Dufraisse and Mackall, *Bull. soc. chim.*, **33,** 934 (1923).

dry ether was added 18.2 g. (0.1 mole) of benzophenone. A very slight heat of reaction which seemed to continue for some time was insufficient to keep the ether rrfluxing. To hasten the reaction, the mixture was refluxed vigorously for six to eight hours. The reaction proceeded smoothly with the formation of the sodium salt of triphenylpropargyl alcohol, which was soluble in ether. When the mixture became a clear solution, the reaction was assumed to be completed but the refluxing was usually continued for an extra hour. The reaction mixture was almost colorless.

After cooling to room temperature, the mixture was poured with stirring into 500 cc. of normal sulfuric acid. Without separating the layers, the ether was allowed to evaporate at room temperature. The light yellow oil which remained was composed of triphenylpropargyl alcohol, phenylacetylene and benzophenone. The mixture was cooled to 0° whereupon the oily layer became a thick sirup. In the course of a few hours at this temperature crystals slowly formed until finally the layer was solid. This solid was broken up and filtered, then washed with petroleum ether and dried. The yield of crude material was 20–22 g., which was 71–74% of the theoretical. One crystallization from benzene and petroleum ether was sufficient to obtain a product which melted at 78–80°. The yield of triphenylpropargyl alcohol thus purified was 16–18 g., or 65–70% of the theoretical.

Trimethylpropargyl Alcohol.—Methylacetylene, prepared from 250 g. of propylene bromide'? and alcoholic potassium hydroxide, was conducted through a long, well-cooled condenser and then through three cold phosphorus pentoxide traps. The dry gas was then passed into a 500-cc. solution of 1.0 mole of ethylmagnesium bromide in ether. The rate of addition of the methylacetylene was such that a gentle but steady refluxing of the ether was induced, with the formation of ethane and methylethinylmagnesium bromide. Although methylacetylene which is prepared from propylene bromide contains some allene, no trouble is caused thereby since the allene cannot react with ethylmagnesium bromide.

The reaction mixture of ether, methylethinylmagnesium bromide and excess ethylmagnesium bromide was cooled to 0° and to it 1 5 moles (87 g.) of acetone was added slowly. The Grignard addition compound was decomposed by cold dilute hydrochloric acid and the ether layer was washed, dried and distilled under reduced pressure. Methyl-2-pentine-3-01-2 was isolated as a colorless liquid boiling at 75–77' (15 mm.). The yield was 47 g. (47% of the theoretical). The index of refraction, n_D^{20}, was 1.4193.

Anal. Subs. 0.2041: CO_2, 0.5472; H_2O, 0.1836. Calcd. for $C_6H_{10}O$: C, 73.4; H, 10 2. Found: C, 73.2; H, 10.2.

Methyl-2-pentene-1-ine-3.—In this synthesis of trimethylpropargyl alcohol, part of the alcohol was always dehydrated with the formation of methyl-2-pentene-1-ine-3, $CH_2{=}C(CH_3){-}C{\equiv}C{-}CH_3$. The yield of hydrocarbon depended on the temperature at which the reaction occurred, and yields as high as 60% were obtained. No efforts were made to improve this yield. No doubt it would he possible to obtain almost quantitative yields by heating the alcohol with oxalic acid dihydrate, since t-butyl alcohol (a related tertiary alcohol) is easily dehydrated in this manner. The methylpentenine was also isolated as a by-product in the preparation of methyl-2-chloro-2-pentine-3, but in much smaller amounts. This hydrocarbon was also one of the chief pyrolytic products of trimethylpropargyl phenyl ether (see below). It was a colorless liquid which boiled at 75–77" and which gave a value of 1.4002 for the index of refraction, n_D^{20}.

Anal. Subs., 0.2148, 0.1407: CO_2, 0.7070, 0.4630; H_2O, 0.3800, 0.1254. Calcd. for C_6H_8: C, 89.94; H, 10.06. Found: C, 89.66, 89.75; H, 9.82, 9.94.

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[17] Hurd, Meinert and Spence, THIS JOURNAL, 52, 1141, second method (1930).

γ-Methylpropargyl alcohol **(butine-2-ol-1)** was synthesized by **Yvon's**[18] method from **trioxymethylene** and methylethinylmagnesium bromide. It was collected in 16% yield at **137–140"**; n_D^{20} **1.4497.** Yvon reported a yield of **25%.** Various modifications were tried with no better success. These included the use of gaseous formaldehyde, the use of an excess of Grignard reagent, or the variation of temperature or time of reaction.

1-Phenylethinylcyclohexanol-1.—Twenty-five grams of freshly distilled phenylacetylene **(0.25** mole) was converted into its sodium salt. To this **was** then added slowly **25** g. **(0.25** mole) of cyclohexanone. A vigorous reaction resulted. Then the mixture was refluxed until a clear solution was obtained after which it was hydrolyzed with dilute hydrochloric acid and the ether layer separated. The water layer was extracted with a small quantity of ether and the ether extracts combined. After drying over sodium sulfate, the solution was fractionated. Eighteen grams of a mixture of phenylacetylene and cyclohexanone was obtained, then 1-phenylethinylcyclohexanol-1 distilled as a thick, colorless sirup, b. p. 166–169° at **14** mm. After several hours at room temperature this material crystallized to a white solid which melted at 58–60°. The yield was **25.1 g.,** or **50%.**

α,γ-Diphenyl-α-p-dimethylaminophenylpropargyl Alcohol.—Sodium phenylacetylide was made from **33** g. of phenylacetylene (0.33 mole), and **75** g. **(0.33** mole) of p-dimethylaminobenzophenone[19] in 150 cc. of benzene was added. The mixture was refluxed until all of the solid had disappeared (four hours). After completion of the reaction, the mixture was poured into cold water and the benzene layer washed to remove the sodium hydroxide formed. The benzene solution was then dried and the solvent distilled. The black, tarry material which remained was extracted with petroleum ether. Most of the impurities were removed by this method. A light colored solid was obtained which, on recrystallization from benzene, gave a fine white crystalline material of m. p. 144–145°. The yield was 55 g., or 50%.

Anal. Subs. **0.2841, 0.4020: 0.100** N HCl, 8.50, **12.20.** Calcd. for $C_{23}H_{21}ON$: **N, 4.28.** Found: **N,** 4.14, 4.22.

The **Propargyl Chlorides—Triphenylpropargyl** chloride was **prepared**[20] from phosphorus trichloride and the alcohol in benzene.

Trimethylpropargyl Chloride.—To a solution of **20.0** g. of **trimethylpropargyl** alcohol (0.2 mole) in **50** cc. of **dry** ether was added **13.7** g. of phosphorus trichloride **(0.1** mole). The reaction mixture was maintained at **0°** for one hour and at room temperature for two hours. After this time the ether solution was decanted from the phosphorous acid and distilled. The fraction which boiled at 35–65° and 47 mm. was collected, washed with cold water, dried and redistilled. Trimethylpropargyl chloride (methyl-2-chloro-2-pentine-3) was obtained as a light yellow liquid, b. p. **57-61°** at **47** mm.; n_D^{20} **1.4143.** The yield was 6.6 **g. (33%).**

Anal. Subs., **0.2358, 0.2510:** cc. of $N/10$ $AgNO_3$, **19.9, 20.4.** Calcd. for C_6H_9Cl: **Cl, 30.43.** Found: **Cl,** 30.48, 30.65.

γ-Methylpropargyl Chloride **(Chloro-1-butine-2).**—To **10.0** g. of **butine-2-ol-1** (0.14 mole), dissolved in **50** cc. of dry ether, was added **10.0** g. of phosphorus trichloride **(0.07** mole). **A** vigorous reaction began immediately and in one hour it was completed. After standing for eight hours at room temperature, the ether solution was decanted from the phosphorous acid, washed quickly with cold water, dried and distilled. **Chloro-1-butine-2** was obtained as a light yellow liquid, b. p. **81–84'.** The yield was **5.4 g.,** which is 44% of the theoretical.

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[18] Yvon, *Compt. rend.*, 180, **749 (1925).**

[19] This material was prepared by Hurd and Webb, THIS JOURNAL, 49, 551 **(1927).**

[20] Moureu, Dufraisse and Mackall, Bull. *soc. chim.*, **33, 934 (1923).**

Anal. Subs. 0.2009, 0.2014: cc. of $N/10$ $AgNO_3$, 23.4, 23.4. Calcd. for C_4H_5Cl: Cl, 40.34. Found: Cl, 41.28, 41.23.

The Phenyl Ethers

Triphenylpropargyl Phenyl Ether.—Five grams (0.015 mole) of triphenylpropargyl chloride was added to 50 cc. of absolute ether. The chloride was only slightly soluble. To this mixture was then added an ether solution containing the sodium phenoxide obtained by treating 2.5 g. of phenol with a slight excess of sodium. A finely divided precipitate of sodium chloride settled to the bottom and a clear solution was obtained. After filtration the ether was evaporated off, thereby leaving a mass of yellow crystals which was washed with cold water and with cold absolute alcohol. The crystalline material was recrystallized from ether; m. p. 90–90.5". The yield of the ether was 70% of the theoretical, or 4.3 g.

Anal. Subs., 0.1628: CO_2, 0.5346; H_2O, 0.0901. Calcd. for $C_{27}H_{20}O$: C, 89.68; H, 5.59. Found: C, 89.54; H, 5.79.

Trimethylpropargyl Phenyl Ether.—An ether solution containing 50 cc. of dry ether, 5 g. (0.04 mole) of trimethylpropargyl chloride and 30 cc. of acetone was made and to it was added 5 g. of potassium carbonate and 3.3 g. (0.04 mole) of phenol. The mixture was refluxed for four hours. Fifty cc. of ether was then added and the ether solution washed with dilute alkali to remove unreacted phenol. The ether solution was dried and fractionally distilled. After removal of the ether and the unreacted trimethylpropargyl chloride, a clear and rather viscous yellow oil remained; n^{20}_{D} 1.3408. All attempts to purify the oil by distillation brought about pyrolysis. The yield was 4.8 g., which was 69% of the theoretical. For identification, its molecular weight was determined.

Mol. wt. Subs. 0.2040; benzene, 21.96; freezing point lowering, 0.150". Calcd. for mol. wt. of $C_{12}H_{14}O$: 174. Found: 340. Subs., 0.1694, 0.2421; acetic acid, 26.23, 26.23; freezing point lowering, 0.150°, 0.220". Found: mol. wt., 167.9, 168.6.

y-Methylpropargyl Phenyl Ether.—Four grams (0.055 mole) of chloro-1-butine-2 was dissolved in 50 cc. of absolute ether, and to this solution were added 5.0 g. of potassium carbonate, 10 cc. of acetone and 4.6 g. (0.055 mole) of phenol. After the first vigorous reaction, the mixture was refluxed for six hours. The ether solution was then carefully washed with dilute alkali to remove unreacted phenol. After washing with water and drying, the mixture was fractionally distilled. γ-Methylpropargyl phenyl ether was obtained as a colorless oil, b. p. 123–126° at 25 mm.; n^{20}_{D} 1.3894. A 57% yield (4.6 g.) was realized in the preparation.

Anal. Subs. 0.1442: CO_2, 0.4340; H_2O, 0.0920. Calcd. for $C_{10}H_{10}O$: C, 82.13; H, 6.90. Found: C, 82.15; H, 7.08.

Pyrolysis of the Ethers

Triphenylpropargyl Phenyl Ether.—One gram of the pure ether was heated in a test-tube by means of a large salt-bath. The temperature was raised slowly and uniformly to 310°. At 230° the compound darkened appreciably. At a bath temperature of 252" the reaction temperature ascended from 248 to 256°, indicating a slight exothermic reaction. The noticeably vigorous change occurred at 295°, however, when the vapor of phenol was evolved in appreciable amounts (0.12 g.). The temperature of 310" was maintained for about ten minutes, which was about five minutes after the evolution of a gas had ceased. Then the bath was allowed to cool slowly to room temperature.

A red, glassy material was obtained which, on pulverizing, became a light yellow powder which fused between 85–98°. By extraction with petroleum ether a soluble portion was obtained which after recrystallization melted at 98–100°. This was 9-

phenylethinylfluorene, and it was formed in 45–50% yields. The fraction which was insoluble in petroleum ether was crystallized from benzene. Less than 0.01 g. of red crystals was obtained, m. p. 240–250°.

Synthesis of 9-Phenylethinylfluorene.—Fluorene in acetic acid was oxidized[21] with sodium dichromate to fluorenone, and the latter reduced[a] in alkaline alcoholic solution to 9-hydroxyfluorene by zinc dust. Thionyl chloride was then used to effect the change into 9-chlorofluorene.[22b] Respectively, the yields in the three operations were 50, 87 and 76%.

A slight excess of sodium was added to 3 0 g. of phenylacetylene in 50 cc. of dry ether. The excess of sodium was mechanically removed after completion of the reaction. To the sodium phenylacetylide thus prepared was added three g. of 9-chlorofluorene (0.015 mole). The mixture immediately assumed a dark brown coloration. It was refluxed for three hours and then the solution was filtered to remove the unreacted sodium phenylacetylide and sodium chloride. Evaporation of the filtrate yielded a brown, crystalline solid. The pure 9-phenylethinylfluorene was readily obtained from this as a yellow solid which melted at 98–100" by crystallization from petroleum ether. The yield was 2 g., or 50%.

Anal. Subs., 0.1627: CO_2, 0.5649; H_2O, 0 0750. Calcd. for $C_{21}H_{14}$: C, 94.69; H, 5.31. Found: C, 94.54; H, 5.19.

Phenylethinylfluorene was also synthesized from the 9-hydroxyfluorene. One gram of the latter was dissolved in 50 cc. of dry ether and to it was added 2 g. of phenylacetylene. The mixture was chilled to 5–10° and 5 cc. of concd. sulfuric acid was added slowly while the solution was stirred vigorously. After washing the solution with a little water to remove the sulfuric acid, the solution was evaporated, leaving crude 9-phenylethinylfluorene as a yellow solid. After recrystallization there was 1 g. of pure product (m. p. 98–100°), which was a 65% yield.

Trimethylpropargyl Phenyl Ether.—In a test-tube which was heated by an oil-bath was placed 3.5 g. of trimethylpropargyl phenyl ether. The test-tube was connected to an efficient condenser and the temperature of the bath was carefully raised. At 160° the substance darkened materially and it was maintained at that temperature for half an hour. A small amount of vapor was at once apparent. This condensed and was collected as a colorless liquid. It proved to be methyl-2-pentene-1-ine-3. The yield of it was 0.8 g., a 43% yield.

The material which remained in the test-tube became a black tar after a few minutes and no further decomposition was evident as the heating was prolonged. Extraction of this tar with alkaline solution yielded 0.35 g. of phenol (as tribromophenol). This was 20% of the theoretical. The tarry, alkali-insoluble residue weighed 2.1 g.

γ-Methylpropargyl Phenyl Ether.—Three grams of y-methylpropargyl phenyl ether was heated slowly in a test-tube immersed in a large oil-bath. The temperature was raised slowly to 215–220° without any apparent decomposition and at this point a natural reflux seemed to occur. After one-half hour at this temperature, the material had become much darker and after one and a half hours it was black. When cooled, a thick, black and tarry material was obtained.

Extraction of the tar thus formed with dilute alkali gave less than 0 1 g. of phenol as tribromophenol. The tar was but slightly soluble in ether whereas benzene dissolved it readily. To ascertain the complexity of the tar, its molecular weight was taken and found to be about 400.

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[21] Graebe and Rateanu, *Ann.*, **297,** 258 (1894).

[22] (a) Barbier, *Compt. rend.*, 80, 1396 (1875); (b) Werner and Grob, *Ber.*, **37,** 2887 (1904).

Mol. wt. Subs., 0.2638, 0.3018, 0.2833; benzene, 21.96, 21 96, 21.96; freezing point lowering, 0.144, 0.169, 0.164°. Mol. wt., 407, 401, 392.

Summary

New syntheses of phenylethinyl phenyl ketone (benzoylphenylacetylene) and of ethyl phenylpropiolate have been developed.

A homolog of propargyl alcohol, $RC{\equiv}C{-}CH_2OH$, and four trisubstituted analogs, $RC{\equiv}C{-}CR_2OH$, were synthesized. Three of these were converted into the corresponding propargyl chlorides and then to the phenyl ethers. These ethers were subjected to pyrolysis.

Triphenylpropargyl phenyl ether pyrolyzed into phenol and 9-phenylethinylfluorene, which was synthesized for purposes of identification from fluorene. Both trimethylpropargyl alcohol and trimethylpropargyl phenyl ether decomposed on heating into phenol and a conjugated "ene–ine" hydrocarbon, namely, methyl-2-pentene-1-ine-3. When refluxed, γ-methylpropargyl phenyl ether changed primarily into a tar, the apparent molecular weight of which was 400. No simple allenes were found although they may have been the precursors of the tars. Should propargyl aryl ethers have been found to rearrange like allyl aryl ethers, allenes would have been expected.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXX. THE ACTION OF OZONE ON URACIL

BY TREAT B. JOHNSON AND ROBERT B. FLINT[1]

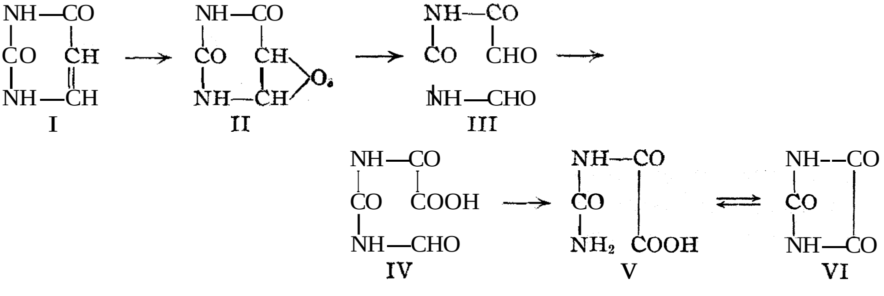
RECEIVED JANUARY 6, 1931 PUBLISHED MARCH 6, 1931

In order to develop a new technique for determining the constitution of nucleic acids, and also known glucosidic combinations containing pyrimidine and purine cycles, the authors decided to investigate the action of ozone on pyrimidines of the uracil type, and to follow this up later with a study of the behavior of certain purines of biochemical interest toward this same reagent. So far as the authors are aware, the behavior of heterocycles of these two types toward ozone has never been investigated. Since both cycles are characterized structurally by the presence of ethylene or unsaturated groupings, it might be predicted that pyrimidines and purines would be very reactive toward ozone, and be broken down at the double bond by this reagent with formation of unique acyclic, ureide constructions possessing immediate biochemical interest. In this paper we now describe the behavior of the pyrimidine "uracil" I when allowed to interact with ozone in glacial acetic acid at ordinary temperature.

[1] Constructed from a dissertation presented by Robert Barnett Flint to the Graduate School of Yale University in June, 1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Uracil I is not readily attacked by ozone in glacial acetic acid or 85% formic acid at ordinary temperature. If, however, the pyrimidine is suspended in either solvent, and washed ozone generated by passing oxygen gas through an ozonizing unit is bubbled into such a suspension for several hours, the uracil is finally completely destroyed and several products are formed as a result of the ozone action. The two major compounds produced are the ureides oxaluric acid V, and formyl-glyoxyl-urea III. Other degradation products formed along with these are urea, oxalic and formic acids and an unknown pyrimidine. The data already obtained indicate that uracil interacts with ozone in a normal manner to form first a true ozonide as expressed by formula II. This addition product is, however, very unstable and all attempts to isolate it were unsuccessful. In both acetic and formic acid solutions it undergoes decomposition rapidly under the experimental conditions employed, giving as the first product of reaction the new ureide *formyl-glyoxyl-urea* as represented by formula III. This represents the chief product of reaction and is the first member of its type to be described. The corresponding ureide acid, formyloxaluric acid IV, has been described by Gorski,[2] who prepared it by interaction of formylurea with oxalic acid.

The second ureide formed in relative amount is oxaluric acid V, which probably results by oxidation and subsequent hydrolysis of formyl-glyoxyl-urea III. The urea, oxalic acid and formic acid formed in the ozone reaction may all be accounted for as resulting from oxidation and hydrolytic changes of this ureide III. The only positive experimental evidence in favor of the formation of a pyrimidine is the response to a murexide color test. The quantity formed is very small, and thus far we have secured no data which would suggest its constitution. These various transformations of uracil are expressed by the formulas



The observation that oxaluric acid V is *a* product of reaction by ozonization of uracil is of biochemical interest as it introduces new chemical evidence in favor of the assumption that this pyrimidine may be one source of oxaluric acid, which is known to be a product of metabolism

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[2] Gorski, *Ber.*, *29*, 2046 (1896).

and has been shown to occur in human urine.[3] The source of this ureide in metabolism has generally been attributed to the destructive oxidation of purines or uric acid. At the present time we have very little information regarding the mechanism of molecular degradation when uracil is oxidized and destroyed in body metabolism.[4]

It is our purpose to determine the generality of this type of change by applying the treatment with ozone to a series of derivatives of uracil. The reaction opens up an important and practical procedure for determining the constitution of pyrimidine compounds belonging to the uracil series.

Experimental Part

Preparation of Uracil.—The uracil used in this research was prepared from urea. malic acid, and fuming sulfuric acid in accordance with a modification of the method developed by Davidson and Baudisch,[5] which has been applied in this Laboratory with success by several workers. Four hundred cubic centimeters of 13% fuming sulfuric acid is cooled to 0° and, while the acid is stirred mechanically, 100 g. of malic acid added at such a rate that the temperature of the mixture does not rise above 5°. After the malic acid has been added, the mixture is cooled to 0° and constantly stirred while 100 g. of finely pulverized urea is rapidly added. The temperature rises rapidly to 50° and at 60° there is a vigorous evolution of carbon monoxide. The temperature of the reaction mixture is maintained at 85° for forty-five minutes, then it is cooled and finally poured over 1200 g. of crushed ice. The uracil is precipitated by this treatment and is completely deposited after twenty-four hours. It is purified by crystallization from hot water. The yield averages about 59% of the theoretical quantity.

Interaction of Uracil with Ozone in Glacial Acetic Acid.—Five grams of uracil is suspended in 100 cc. of glacial acetic acid and ozonized oxygen, previously washed with a 5% aqueous solution of sodium hydroxide and finally with concentrated sulfuric acid, is bubbled through the suspension for fourteen to sixteen hours. The uracil slowly dissolves and at the end of the reaction period only a light suspension of crystalline material remains undissolved in the acetic acid. As the reaction approaches completion, the suspended material is tested at fifteen-minute intervals for the presence of uracil by the Wheeler and Johnson[6] method employing bromine water and barium hydroxide. When the characteristic purple precipitate no longer appears after this treatment, the ozone transformation is considered complete. Our methods of separating and identifying the products of this reaction are described below.

Identification of Oxaluric Acid, V.—The reaction product, which was insoluble in the acetic acid after completion of the ozone treatment (above), weighed 0.6 g., and it melted before purification at 183–187° with decomposition. After purification by recrystallization from 95% alcohol, in which it is difficultly soluble, or from glacial acetic acid, it decomposed when heated at 205–215°. It was difficultly soluble in water, but was soluble in alkaline solution and interacted to form insoluble barium and silver salts. Ammonia was evolved when the ureide was warmed in alkaline solution and oxalic acid was shown to be formed by hydrolysis. Urea was also identified in the solution by means

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[3] See Schunck, Jahresb., 749 (1866).

[4] See Cerecedo, *J. Biol. Chem.*, **75**, 661 (1927); Emerson and Cerecedo, *ibid.*, **87**, 453 (1930).

[5] Davidson and Baudisch, THIS JOURNAL, **48**, 2379 (1926).

[6] Wheeler and Johnson, *J. Biol. Chem.*, **3**, 183 (1907).

of the Fossc[7] xanthydrol reagent. In fact, the compound agreed in all its properties with those described for oxaluric acid by Biltz and Topp.[8]

Anal. Calcd. for $C_3H_4O_4N_2$: N, 21.21. Found: N, 21.07, 20.91.

The identity of this ureide was further confirmed by the formation of its ethyl ester, which was prepared by digesting the acid in alcohol acidified with sulfuric acid. The ester separated in the form of needles and after purification by crystallization from ether it melted at 177° with decomposition.

Anal. Calcd. for $C_5H_8O_4N_2$: N, 17.50. Found: N, 17.57.

Identification of Formyl-glyoxal-urea, 111.—After separation of the oxaluric acid by filtration (ozone–uracil reaction), the acetic acid was removed by heating at 50°, when we obtained 4.5 g. of a colorless crystalline substance. This was apparently a mixture of several products and all attempts at purification by crystallization from alcohol, chloroform, benzene, ethyl acetate and ether were unsuccessful. By use of hot, glacial acetic acid we succeeded in separating 2.4 g. of a definite crystalline substance which melted constantly at 162°. This was characterized by the following properties: solubility in water, giving a solution which reacted acid to litmus and in 95% alcohol and also dilute potassium carbonate solution; insoluble in ether, benzene and chloroform.

No insoluble barium salt was formed by the action of barium hydroxide, but addition of silver nitrate to an alkaline solution of the compound gave immediately a colorless, flocky precipitate of a silver salt. The warming of a solution of this silver salt in ammoniacal solution led to the production of a bright silver mirror on the walls of the glass receptacle. The silver salt was prepared by precipitation in neutral solution, washed with water, alcohol and ether and finally dried at 80°. This gave on analysis the following results for nitrogen and silver.

Anal. Calcd. for $C_4H_3O_4N_2Ag{\cdot}H_2O$: N, 10.41; Ag, 40.14. Found: N, 10.38; Ag, 39.98.

The compound melting at 162° reduced Fehling's solution immediately on warming and also interacted with Tollens' reagent to form *a* silver mirror, but there was no apparent reaction with Schiff's reagent. Application of the murexide test was negative and it produced no color when introduced into ferric chloride solution, proving that we were not dealing here with formylallanturic acid.[9] The compound was decomposed by digestion with dilute sulfuric acid with formation of formaldehyde and urea. Some of the compound melting at 162° was warmed with dilute nitric acid and the solution then evaporated to dryness. In this residue was easily identified oxalic acid. This exhaustive study of the properties of this substance formed from uracil by the action of ozone led us to conclude that we were dealing with the hitherto unknown acyclic ureide, *viz.*, *formyl-glyoxyl-urea*, 111 The identity of the compound was further established by analysis.

Anal. Calcd. for $C_4H_4O_4N_2$: C, 33.33; H, 2.8; N, 19.44. Found: C, 33.52; H, 3.0; N, 19.37, 19.33.

An attempt to prepare a phenylhydrazone of formyl-glyoxyl-urea was unsuccessful. The ureide interacted with phenylhydrazine in acetic acid solution at ordinary temperature giving a product which melted after purification at 144–145°. It crystallized from alcohol in colorless plates and was identified as formylphenylhydrazine.[10]

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[7] Fosse, *Ann. chim.*, [9] *6*, 13 (1916).

[8] Biltz and Topp, *Ber.*, 46, 1408 (1913).

[9] Behrend and Griinewald, *Ann.*, 323, 201 (1902).

[10] Vries, *Ber.*, 27, 1522 (1894); Ramberger, *ibid.*, 30, 1264 (1897); Claisen, *Ann.*, 287, 370 (1895).

Anal. Calcd. for $C_7H_8ON_2$: N, 20.59. Found: N, 20.49.

An attempt to prepare the phenylhydrazone by interaction in absolute alcohol was also unsuccessful. The reaction was applied with 5 cc. of phenylhydrazine, 65 cc. of alcohol and 0.5 *g.* of formyl-glyoxyl-urea. This solution was digested on the steam-bath for three hours, cooled and then diluted with water, when a crystalline substance separated on standing. This was purified by crystallization from absolute alcohol and separated in the form of yellow needles decomposing at 221°. A nitrogen determination by the Dumas method gave a value of 29.5%. In sodium hydroxide solution this dissolved with formation of a deep blue coloration which was discharged by acidification with hydrochloric acid. On adding alkali the blue color was regenerated. Behrend and Grünewald[9] have described a phenylhydrazine derivative of acetylallanturic acid which possesses similar properties. The structure of this compound will be determined and discussed in a later paper.

The acetic acid filtrate from which formyl-glyoxyl-urea was separated by crystallization was examined further for secondary products of ozonization. The possibility of the presence of an ozonide here was eliminated by the fact that no iodine was liberated when the residue obtained after evaporation of the acetic acid was treated with potassium iodide. The presence of oxalic acid and urea was easily detected, and we also observed that this residue gave a pronounced murexide test, indicating the presence of an unknown pyrimidine combination. We were unable, however, to separate a definite pyrimidine combination from this residue.

Formation of Formyl-glyoxyl-urea from Uracil by the Action of Ozone in 85% Formic Acid Solution.—Five grams of uracil was suspended in 100 cc. of 85% formic acid and ozonized oxygen bubbled through the suspension for twenty-three hours. The uracil dissolved and was completely destroyed by action of the ozone. After evaporating the formic acid solution at 50" we obtained a crystalline residue containing urea, oxalic acid and formyl-glyoxyl-urea. Two grams of the latter ureide melting at 162" was obtained by fractional crystallization from glacial acetic acid. This corresponds to a yield of 31% of the theoretical. By ozonization of uracil in glacial acetic acid the yield of this ureide is raised to 38% of the theoretical.

Summary

1. Uracil and ozone interact in glacial acetic acid at ordinary temperature to form chiefly two compounds, *viz.*, formyl-glyoxyl-urea and oxaluric acid.

2. Part of the uracil molecule is completely broken down with formation of urea, oxalic and formic acids.

NEW HAVEN, CONNECTICUT

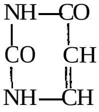
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXXI. THE ACTION OF OZONE ON SOME DERIVATIVES OF URACIL

BY TREAT B. JOHNSON AND ROBERT B. FLINT[1]

RECEIVED JANUARY 6, 1931 PUBLISHED MARCH 6, 1931

In the previous paper from this Laboratory dealing with pyrimidine chemistry,[2] the authors described the behavior of uracil I toward ozone. It was shown that this pyrimidine cycle can be broken down by the action of ozone without destruction of the ureide structure, and with formation of definite oxidation products characteristic of the constitution of uracil. The characteristic ureides produced by ozonization were identified as oxaluric acid III and formyl-glyoxyl-urea II. Besides these two ureides practically the only other products of reaction were urea, formic and oxalic acids. The definite course of the reaction, its ease of application, and the character of the products formed by decomposition of the pyrimidine were so promising that it seemed desirable to study the action of ozone on other derivatives of uracil. Any transformations of this character, which will serve for determination of the constitution of uracil derivatives, should prove of immediate practical value in many of our problems dealing with cell chemistry, and now calling for solution. In this paper we describe new applications of this reaction, and report on the action of ozone on 4-methyluracil, 4-phenyluracil, thymine, 5-bromouracil, 5-nitrouracil and 1,3-dimethyl-5-bromouracil.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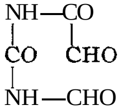
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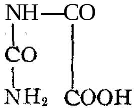
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As in the case of uracil, all these pyrimidines interact with ozone in glacial acetic acid at ordinary temperature with destruction of the pyrimidine ring, but without complete degradation of the molecule. The ureide configuration of the original pyrimidine is preserved in some form in every case. As already known, 4-methyluracil is attacked by potassium permanganate in acid solution with formation of trihydroxydihydromethyluracil which Behrend and Osten[3] showed is transformed by more intensive oxidation into acetyloxaluric acid V and finally acetylurea and oxalic acid. With ozone 4-methyluracil reacts also with ring cleavage giving a 67% yield of acetyl-glyoxyl-urea represented by formula VI.

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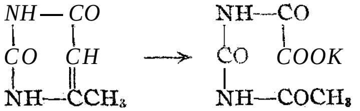
[1] Constructed from a dissertation presented by Robert Barnett Flint to the Graduate School of Yale University in June, 1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Johnson and Flint, THIS JOURNAL, 53, 1077 (1931).

[3] Behrend and Osten, *Ann*, 343, 133 (1905)

No evidence was obtained of the formation of oxaluric acid, as was observed in the case of uracil, or any acetyl-oxaluric acid V.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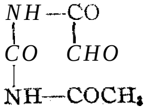
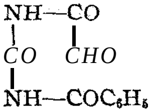

VI

4-Phenyluracil reacts with ozone to give the corresponding benzoylglyoxylurea VII, while thymine underwent a more intensive degradation under similar experimental conditions, giving an excellent yield of formylurea VIII. In this respect the thymine degradation corresponds to that of 4-methyluracil, which has been shown to break down by intensive oxidation with potassium permanganate, giving acetyl-urea. Pyruvic acid, $CH_3COCOOH$, if formed in the ozonization of thymine, was apparently destroyed by oxidation, as delicate tests for this ketone acid did not reveal its presence in the reaction mixture. Urea was formed to some extent in all cases examined and was easily detected by means of Fosse's reagent, "xanthydrol."[4]

Especially interesting was the behavior of 5-bromouracil, 5-nitrouracil, and 1,3-dimethyl-5-bromouracil toward ozone. The only one of these three derivatives which favored the formation of an acylic ureide was 1,3-dimethyl-5-bromouracil. This gave an oxidation product having the composition and properties of dimethyloxaluric acid, IX. We did not succeed in detecting in the reaction mixture any cholestrophan or dimethyl-parabanic acid. The corresponding monomethyl-oxaluric acid has been shown to be formed by oxidation of α- and β-dimethyluracil with potassium permanganate.[6] 5-Bromouracil, on the other hand, reacted with ozone under similar conditions giving an excellent yield of parabanic acid, while 5-nitrouracil was decomposed to form urea, oxalic acid and the two ureides, parabanic acid and oxaluric acid.

Ring closure to form parabanic acid in the ozonization of 5-bromouracil and 5-nitrouracil represents only the end of a series of reactions. After removal of this cycle from the reaction products, both residues responded to qualitative tests indicating the presence of formyl-oxaluric acid. Formic acid, urea and oxalic acid were identified after hydrolysis, but we were unable to separate the formyl-oxaluric acid in either case.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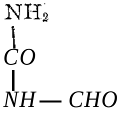
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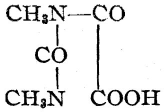
IX

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[4] Fosse, Ann. *chim.*, [9] 6, 13 (1916).

[5] Behrend and Dietrich, Ann., 309,271 (1899).

Experimental Part

In studying the action of ozone on the pyrimidines incorporated in this research we have operated according to a general procedure, as follows. A definite quantity of the respective pyrimidine is suspended in a known volume of glacial acetic acid and dry ozonized oxygen is then bubbled through the suspension at ordinary temperature until the transformation of the respective pyrimidine is complete. In the majority of cases solution of the pyrimidine in the acetic acid takes place very slowly, and it is necessary to pass ozone through the acid solution for several hours before the reaction is brought to completion. Acetic acid has proved to be the best solvent for our work; no products of reaction are formed which discolor the acid, and also no resinous substances are produced which interfere with the identification of the characteristic products of reaction.

The Action of Ozone on 4-Methyluracil, IV.—The methyluracil which was used in this research was made according to the directions of Biltz and Heyn[6] by condensing ethyl acetoacetate with urea in the presence of hydrochloric acid. The proportions used during ozonization were 5 g. of the pyrimidine and 100 cc. of glacial acetic acid. The pyrimidine suspended in the acetic acid slowly dissolves during the ozone treatment, and at the end of fourteen hours the reaction is complete and a clear colorless solution is obtained. On allowing this solution to evaporate in a current of air at 50° until the acetic acid was removed, we obtained a crystalline residue which weighed 6.0 g. Purification was effected by crystallization from absolute alcohol, when we succeeded in separating 4.2 g. of a crystalline substance which melted at 150°. Repeated crystallizations failed to raise this melting point. This was identified as ***acetyl-glyoxyl-urea*** and the yield obtained corresponded to 67% of the theoretical.

Anal. Calcd. for $C_5H_6O_4N_2$: N, 17.72. Found: N, 17.40, 17.52, 17.44.

Acetyl-glyoxyl-urea is soluble in water and moderately soluble in 95% alcohol and glacial acetic acid. It is insoluble in ether, benzene, chloroform and ethyl acetate. An aqueous solution of the ureide gives no precipitate of calcium oxalate when warmed in ammoniacal solution with calcium chloride. The ureide reduces Fehling's solution immediately on warming and reacts with Tollens' reagent to form a silver mirror and gives no blue color with ferric chloride. Five-tenths of a gram of the ureide was warmed in dilute hydrochloric acid solution, when it was completely decomposed with formation of urea. The latter was identified by precipitation with xanthydrol according to Fosse's[4] method. The same experiment was repeated, but with the addition of a small amount of nitric acid. Under these conditions complete hydrolysis took place with formation of urea and also oxalic acid, which was identified by precipitation as calcium oxalate.

The alcohol filtrate from which acetyl-glyoxyl-urea was separated by crystallization was found to contain free urea and oxalic acid. We obtained no evidence in this case of the formation of oxaluric acid, as was observed when uracil was treated with ozone.[2]

The Action of Ozone on 4-Phenyluracil.—4-Phenyluracil was synthesized according to the directions of Johnson and Hemingway[7] by condensation of thiourea with ethyl benzoylacetate, when 2-thio-4-phenyl-6-oxypyrimidine is formed. Desulfurization of the latter pyrimidine by the action of chloroacetic acid yields quantitatively the 4-phenyluracil melting at 270°. The proportions used for ozonization were 5 g. of the

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[6] Biltz and Heyn, **Ann.**, 413, 109 (1917).

[7] Johnson and Hemingway, THIS JOURNAL, 37, **378** (1915)

pyrimidine and 100 cc. of glacial acetic acid. The pyrimidine suspended in the acetic acid interacts readily with ozone and at the end of seven hours a colorless solution was obtained and the pyrimidine ring was completely destroyed. The acetic acid was then removed by evaporation in a current of air at 50°, when we obtained a sirupy residue which we again dissolved in 10 cc. of glacial acetic acid, and allowed to stand in an ice chest for about twelve hours. Two grams of a crystalline compound separated in the form of prisms which melted at 168°. This was identified as benzoyl-glyoxyl-urea. This ureide is insoluble in cold water, chloroform, benzene and ether, and soluble in hot water, alcohol and ethyl acetate.

Anal. Calcd. for $C_{10}H_8O_4N_2$: N, 12.73 Found: N, 12.80, 12.61.

This ureide reacted in a normal manner with Fehling's and Tollens' solutions, showing the presence of an aldehyde group in the compound. No oxalic acid was produced by hydrolysis with hydrochloric acid, but benzoic acid was easily identified, and separated on cooling in colorless crystals melting at 122°. Urea was separated and identified by means of Fosse's reagent (xanthydrol). When nitric acid was added to the hydrochloric acid and the ureide then subjected to hydrolysis, oxalic acid was formed as a product of reaction. This was identified by precipitation as calcium oxalate.

Action of Phenylhydrazine on Benzoyl-glyoxyl-urea.—One-half gram of the ureide was dissolved in a mixture of 5 cc. of phenylhydrazine, 5 cc. of 50% acetic acid and 15 cc. of water. There was a reaction at ordinary temperature and on standing a crystalline substance separated. After purification by crystallization from alcohol, this melted at 168" and was identified as benzoylphenylhydrazine.[8] A mixture of this substance and benzoylphenylhydrazine prepared according to Fischer's directions melted at the same temperature.

Anal. Calcd. for $C_{13}H_{12}ON_2$: N, 13.21. Found: N, 13.22.

After separation of the benzoylphenylhydrazine, the reaction mixture was allowed to stand at room temperature for several days, when a yellow substance separated which was purified by crystallization from boiling absolute alcohol. It separated, on cooling, in the form of yellow needles which melted at 221°. This compound was found to be identical with the substance obtained by interaction of phenylhydrazine with formyl-glyoxyl-urea,[2] and also with acetyl-glyoxyl-urea described above. No change in the melting point (221°) was produced when mixtures of the three different preparations were heated in capillary tubes.

The Action of Ozone on Thymine.—The proportions used for the ozone reaction were 3.5 g. of the pyrimidine suspended in 50 cc. of glacial acetic acid. The thymine was attacked immediately by the ozone and after bubbling ozonized oxygen through the suspension for five hours, the thymine had dissolved and was completely decomposed. The acetic acid was then evaporated as usual in a stream of air at 50°, when we obtained 2.6 g. of a semi-crystalline residue. From this was separated by crystallization from absolute alcohol 1.0 g. of formylurea, corresponding to a yield of 40% of the theoretical. It melted at 168°.[9] When this ureide was dissolved in dilute sulfuric acid, urea was formed, and when the vapor evolved on distillation was conducted into a solution of silver nitrate, there was an immediate reduction with formation of metallic silver. Urea was also produced by digesting the ureide in aqueous solution.

Anal. Calcd. for $C_2H_4O_2N_2$: N, 31.82. Found: N, 31.62, 31.73.

The alcohol filtrates obtained after purification of formylurea were combined and evaporated to dryness. In this residue was detected urea by precipitation with xan-

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[8] Fischer, *Ann.*, 190, 125 (1878).

[9] Gorski, *Ber.*, 29, 2046 (1896).

thydrol. Baudisch's[10] test for pyruvic acid failed to reveal the presence of this ketone acid, indicating that it had been destroyed by oxidation.

Action of Ozone on **5-Bromouracil.**—Ozone reacted immediately with bromouracil when bubbled through a suspension of 5.0 g. of the pyrimidine in 100 cc. of glacial acetic acid. Bromine was liberated in this reaction and at the end of eleven hours the bromouracil was completely destroyed. After evaporation of the acetic acid there was obtained 3.6 g. of a crystalline residue from which we obtained by crystallization from acetic acid 1.2 g. of parabanic acid melting with decomposition at 238 to 244°.

Anal. Calcd. for $C_3H_2O_3N_2$: N, 24.56. Found: N, 24.55, 24.42.

In the filtrate left after crystallization of the parabanic acid was detected urea and oxalic acid. We did not succeed in identifying formylurea or oxaluric acid as products of the reaction.

Action of Ozone on **5-Nitrouracil.**—5-Nitrouracil was prepared according to the directions of Johnson and Matsuo[11] and treated with ozone according to the technique already described. The action of ozone was very slow and it required twenty-eight hours before the complete destruction of 3 g. of nitrouracil was accomplished. Evaporation of the acetic acid gave 2.3 g. of a crystalline residue which yielded after washing with alcohol and water 0.5 g. of oxaluric acid decomposing at 205–215°.

Anal. Calcd. for $C_3H_4O_4N_2$: N, 21.21. Found: N, 21.10.

From the alcohol extract was separated by crystallization 1.3 g. of a crystalline substance which yielded by further purification 1.0 g. of parabanic acid melting at 238–242°. When mixed with pure synthetic parabanic acid no change in melting point was observed.

Anal. Calcd. for $C_3H_2O_3N_2$: N, 24.56. Found: N, 24.48.

Urea was also detected in the final residues by means of the Fosse reagent (xanthydrol).

The Action of Ozone on **1,3-Dimethyl-5-bromouracil.**—This bromine derivative of 1,3-dimethyluracil is easily obtained by direct bromination of the dimethylppimidine in aqueous solution, and was obtained in the form of prisms melting at 186°. Johnson and Clapp[12] reported a melting point of 181–182°. Ownization of this pyrimidine (2.8 g.) was not complete under twelve to thirteen hours' treatment. The liberation of bromine was noticeable during the change and after evaporation of the acetic acid a residue of 1.4 g. was obtained. The only products identified were urea, oxalic acid and the hitherto unknown ureide *dimethyl-oxaluric acid.* This was purified by crystallization from absolute alcohol and melted at 124–125°. The acid is soluble in water and glacial acetic acid.

Anal. Calcd. for $C_5H_8O_4N_2$: N, 17.50. Found: N, 17.55.

Summary

1. The behavior of 4-methyluracil, 4-phenyluracil, thymine, 5-bromouracil, 5-nitrouracil and 1,3-dimethyl-5-bromouracil toward ozone has been investigated.

2. In every case the pyrimidine ring is destroyed with formation of characteristic ureide constructions and simple oxidation products. In no case is the urea configuration of the respective pyrimidines destroyed by the ozone treatment.

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[10] Baudisch, THIS JOURNAL, 45, 2978 (1923).

[11] Johnson and Matsuo, *ibid.*, 41, 783 (1919).

[12] Johnson and Clapp, *J. Biol. Chem.*, **5**, 49 (1909).

3. The application of ozonization makes possible an improved technique for determining the structure of uracil compounds. The advantages gained experimentally become apparent when one is called upon to separate and identify the products of oxidation.

4. The urea configuration of the pyrimidine nucleus is not destroyed by the action of ozone.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, HOLY CROSS COLLEGE]

THE EFFECT OF SUBSTITUENTS ON CERTAIN PHYSICAL PROPERTIES OF BENZENE PICRATE[1]

BY O. L. BARIL AND E. S. HAUBER

RECEIVED JANUARY 6, 1931 PUBLISHED MARCH 6, 1931

Only a few of the aromatic hydrocarbons may be identified from their picrates. The reason for this is that very few aromatic hydrocarbons form picrates which are stable and can be purified by crystallization from suitable solvents. Most of the aromatic hydrocarbons form picrates which are decomposed by solvents or on standing in air.

The influence of substituents on the color of benzene picrate was studied by Franzen.[2] From a study of the absorption spectrum of a mixture of picric acid and a number of aromatic hydrocarbons and their halogen derivatives, he found that an increase in the number of alkyl groups in general causes an increase in the depth of the color produced. He also found that m-derivatives are the brightest, and that *p*-derivatives are the darkest.

Compounds of picric acid with aromatic hydrocarbons were studied by Efrenov[3] by means of thermal analysis of the binary mixtures. He found that molecular quantities of the substances usually reacted, but diphenyl, diphenylmethane and triphenylmethane do not give picrates.

Kendall[4] explains the existence of the picrates by the formation of oxonium salts. The existence and stability of the addition compounds were determined from the freezing-point curve. The melting point was determined by distectic points on the fusion curve, *i.* e., the temperature at which crystallization begins. The molecular composition of the picrates was found to be of the general type 1:1.

In our study with picrates, we have prepared the picrates of several

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[1] Some of the experimental results described in this paper are taken from a thesis submitted to the Faculty of Holy Cross College by E. S. Hauber in partial fulfilment of the requirements for the degree of Master of Science.

[2] Hartig Franzen, *J. prakt. Chem.*, 98, 67-80 (1918).

[3] N. N. Efrenov, J. Russ. *Phys.-Chem. Soc.*, 50, 1, 372-421 (1918).

[4] Kendall, THIS JOURNAL, 38, 1314 (1916).

aromatic hydrocarbons, and have taken a melting point of the picrate formed before decomposition took place. The colors of the picrates in the same series were compared in an effort to determine whether or not the substitution of different groups on the benzene ring had any effect on the color of the picrate. In preparing the picrates, a method was used which may be applied to the preparation of picrates of all aromatic hydrocarbons. Wherever possible, the color and the melting points of these picrates were compared with those which could be prepared and purified by crystallization from suitable solvents.

Experimental

All temperatures given are uncorrected.

Picric acid containing 3% of water was dried in an oven at 100° for six hours. All liquid hydrocarbons were dried over anhydrous calcium chloride for twenty-four hours and were freshly distilled. Solid hydrocarbons were crystallized from suitable solvents until they gave a sharp melting point. Equimolecular quantities of the hydrocarbon and picric acid were heated until fusion took place. The melting point of the addition compound was the temperature at which crystallization began, which is in reality the freezing point. The method for the determination of the freezing point was that of Beckmann. A large test-tube containing the two constituents was placed under a reflux condenser. The test-tube was surrounded by a larger test-tube immersed in a bath of concentrated sulfuric acid. The temperature of the sulfuric acid bath was cooled, after fusion took place, at the rate of about one-half a degree per minute below 100°, and at about one to two degrees per minute above 100°. Three determinations were made of each picrate. Wherever possible, these picrates were compared in color and melting point to picrates prepared according to Mulliken.[5] Many picrates prepared could not be found in the literature.

General Procedure.—Ten millimoles of the hydrocarbon and ten millimoles of picric acid were intimately mixed in a test-tube and placed under a reflux condenser. A thermometer was inserted in the mixture. The mixture was gently heated in the sulfuric acid bath until fusion took place, and the bath was then cooled slowly. The freezing point of the picrate was taken on solidification of the mixture. The same mixture was liquefied and the freezing point taken three times in succession in order to check on compound formation.

Aliphatic Derivatives **of** Benzene.—The picrates of the aliphatic derivatives of benzene were prepared from equimolecular amounts of the hydrocarbon and picric acid according to the Beckmann method.

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[5] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1916, Vol. 2, p. 33.

They were also prepared by crystallizing the picrate from a boiling saturated solution of picric acid in the hydrocarbon according to Fritzsche.[6]

TABLE I

ALIPHATIC DERIVATIVES OF BENZENE PICRATE

Substance	Color	Form	M. p., °C.
Benzene	Colorless	Needles	83.9
Toluene	Light yellow	Plates	88.2
Ethylbenzene	Light yellow	Plates	96.6
Propylbenzene	Yellow	Plates	103.5
o-Xylene	Lemon-yellow	Needles	88.5
m-Xylene	Lemon-yellow	Needles	90–91.5
p-Xylene	Lemon-yellow	Needles	90.5
Hemimellitine	Yellow	Needles	89.5
Pseudocumene	Yellow	Needles	96–97
Mesitylene[a]	Bright yellow	Leaflets	96.6
1,2,3,4-Tetramethylbenzene[b]	Golden-yellow	Prisms	92–95
Pentamethylbenzene[c]	Golden-yellow	Prisms	131
Hexamethylbenzene[d]	Orange-yellow	Plates	170

[a] Schultz, Wurth, *Chem. Centr.* I, ***1443*** (1905). [b] This stable picrate crystallizes from boiling alcohol [A. Tohl, ***Ber.***, 21, 905 (1888)]. [c] This stable picrate crystallizes from boiling alcohol [Jacobson, ***ibid.***, 20, 898 (1887)]. [d] This picrate loses hexamethylbenzene at 100–110°. Alcohol removes picric acid. Friedel and Crafts [*Ann. chim.*, [6] **10**, 417 (1887)].

The picrates in Table I are all unstable, decomposing in air, excepting the tetra-, penta- and hexamethylbenzene picrates, which decompose slightly above their melting points. The position of the methyl groups in dimethylbenzene does not have any appreciable effect on the color of the picrates. Separation of the methyl groups in trimethylbenzene raises the melting point of the picrate.

The isomers of the polymethylbenzenes such as cumene and *p*-cymene form no picrates, as all attempts to prepare them failed.

Benzene derivatives containing a double bond in the side chain such as styrene and indene form very explosive picrates.

Hydroxy Derivatives of Benzene.—The hydroxy derivatives of benzene yield picrates which crystallize into beautiful yellow to red crystals from a deep red solution. These equimolecular compounds are highly dissociated on fusion, as is evidenced by the flatness of the maximum on the freezing point curve.[7]

The picrates of the hydroxy derivatives of benzene were prepared from equimolecular amounts of the hydrocarbon and picric acid according to the Beckmann method. All formed needle crystals.

Naphthalene and Anthracene Derivatives.—The picrates of the naphthalene and anthracene derivatives were prepared from equimolecular

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[6] Fritzsche, ***Jahresb.***, 456 (1857).

[7] Kendall, THIS JOURNAL, 38, 1314 (1916).

TABLE II

HYDROXY DERIVATIVES OF BENZENE PICRATE

Substance	Color	M. p., °C
Phenol	Yellow	83.1
Pyrocatechol	Orange-yellow	122
Resorcinol[a]	Orange-yellow	89–90
Hydroquinone[b]	Light yellow	115–117
Pyrogallol	Lemon-yellow	128–129
Hydroxyquinol	Orange-red	96
Phloroglucinol	Brown	101–103
o-Cresol	Orange-yellow	88
m-Cresol[c]	Yellow	61.6
p-Cresol[d]	Bright red	64-65
Orcinol	Orange-yellow	92
1,2,4-Xylenol[e]	Chrome-yellow	83.8
1,3,2-Xylenol	Orange-yellow	50-53
1,4,2-Xylenol	Orange	81–82

[a] Decomposed by water, ethyl ether and ethyl alcohol. [b] Decomposed by benzene. [c] Decomposes in air, ethyl alcohol, ethyl ether and benzene. [d] Unstable at its maximum, m. p. 65.6' by extrapolation. [e] Can be crystallized from alcohol.

TABLE III

DERIVATIVES OF NAPHTHALENE AND ANTHRACENE PICRATES

Substance	Color	Form	M. p., °C.
Naphthalene[a]	Yellow	Needles	149
α-Methylnaphthalene	Lemon-yellow	Needles	140–141
β-Methylnaphthalene	Lemon-yellow	Needles	115–116
α-Ethylnaphthalene	Lemon-yellow	Needles	97.4
β-Ethylnaphthalene	Yellow	Needles	69–70
α-Propylnaphthalene	Yellow	Needles	140–141
β-Propylnaphthalene	Yellow	Needles	89–90
α-Butylnaphthalene	Orange-yellow	Needles	104–105
β-Butylnaphthalene	Orange-yellow	Needles	71–73
1,4-Dimethylnaphthalene	Orange-yellow	Prisms	139–140
2,6-Dimethylnaphthalene	Orange-yellow	Needles	141–142
1,2,6-Trimethylnaphthalene	Orange-yellow	Needles	121–122
α-Naphthol	Orange-yellow	Needles	188.5
β-Naphthol	Orange-yellow	Needles	155.5
Anthracene	Ruby-red	Needles	138
Hexamethylanthracene	Dark brown	Needles	203
Phenanthrene	Orange-yellow	Needles	132.8
Acenaphthene[b]	Orange-red	Needles	160.5
Stilbene[c]	Red	Needles	90–91
Fluorene[d]	Red-brown	Prisms	77
Pyrene	Red	Needles	220

[a] This picrate crystallizes from ethyl acetate in yellow prisms and plates, from ethyl ether in yellow crystals, and from ethyl alcohol in monoclinic prisms and needles. [b] Flat needles from ethyl alcohol. [c] Red needles from alcohol or ether. Decomposes on fusion at 92.8". [d] This picrate crystallizes from ethyl ether in red-brown prisms, and it is unstable.

amounts of the hydrocarbon and picric acid according to the Beckmann method. The picrates were also prepared from a solution of the hydrocarbon and picric acid in boiling alcohol, and their physical properties were compared with the physical properties of the picrates prepared according to the Beckmann method. The colors and melting points of the corresponding picrates were found to be identical.

Although the melting points of the β-naphthalene derivatives are higher than those of the α-naphthalene derivatives, the β-naphthalene picrates have a lower melting point than the corresponding a-naphthalene picrates.

Summary

The addition of hydroxyl groups to benzene picrate lowers the melting point and deepens the color of the picrate formed. The addition of methyl groups to benzene picrate raises the melting point of the product and deepens the color of the picrate less than the hydroxyl group. The addition of methyl groups to a side chain of benzene picrate gradually increases the melting point and deepens the color of the picrate, and this increase is more rapid than when a corresponding number of methyl groups are substituted in the ring. The symmetrical trihydroxy- and trimethylbenzene picrates are the darkest, and the color of the picrates becomes lighter as we approach the 1,2,3-derivatives. The same deepening in color was obtained with the methyl derivatives of naphthalene. The β-naphthalene picrates possess lower melting points than the α-naphthalene picrates. Unsaturation in the side chain yields a very unstable picrate. The heavier the molecule the deeper the color of the picrate.

WORCESTER, MASSACHUSETTS

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS OVER COPPER CHROMITE

BY HOMER ADKINS AND RALPH CONNOR

RECEIVED JANUARY 9, 1931 PUBLISHED MARCH 6, 1931

Nickel has been the only base metal catalyst which has offered much promise for the hydrogenation of pure organic compounds in the liquid phase, although several oxides and mixtures of oxides have been used for the hydrogenation of carbon monoxide in the gas phase at temperatures above 300°. In connection with a study of the action of some of these oxides in inducing the condensation of acetaldehyde at 360°,[1] it seemed advisable to investigate them with respect to their efficiency for catalyzing hydrogenations in the liquid phase. This latter study has resulted in the discovery that a combination of copper and chromium (oxides) is in many

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[1] **Adkins,** Kinsey and **Folkers,** *Ind. Eng. Chem.,* **22,** 1046 **(1930).**

ways very much superior to any catalyst known to the authors for the hydrogenation of several types of organic compounds.

The catalyst used in this investigation was prepared by decomposing copper ammonium chromate. This procedure is described for the preparation of catalysts containing a "hydrogenating metal" and chromium by Lazier.[2] The examples cited in the patents involve the use of the catalysts zinc and manganese chromite for the reaction of carbon monoxide and hydrogen in the vapor phase at 300 atmospheres and 400° to form methanol and higher alcohols.

Preparation of Catalyst.—Ammonium hydroxide was added to a solution of 126 g. (0.5 mole) of ammonium dichromate (Mallinckrodt) in 500 ml. of water until the color of the solution changed from orange to yellow. The volume of the solution was now 650 ml. The solution was allowed to come to room temperature and a solution of 241.6 g. (1.0 mole) of cupric nitrate trihydrate (Mallinckrodt) in 300 ml. of water was added with stirring. The red-brown precipitate was filtered with suction and dried overnight in an oven at 100–110°. It was then finely powdered, transferred to a porcelain casserole, and decomposed by heating the casserole in the flame of a Bunsen burner. After decomposition had begun, the heat of reaction was sufficient almost completely to decompose the chromate. When spontaneous decomposition had ceased, the casserole was heated with the free flame until fumes ceased to be evolved and the contents was black and so finely powdered as to be almost like a liquid. During this heating, care was taken to keep the material well stirred and to rotate the flame in order to avoid local superheating. The product was allowed to cool and then suspended in 200 ml. of a 10% solution of acetic acid. The suspension was filtered with suction, washed thoroughly with water, dried for twelve hours in an oven at 100–110°, and finely powdered. The yield of catalyst was 113 g.

Experimental Results.—There is recorded in Table I a summary of the data obtained in hydrogenating a representative list of 21 organic compounds. There are given in Columns 1, 2 and 3 the names and amounts of compound subjected to the action of hydrogen and the weight of catalyst. In five or six cases the amount of catalyst used (4 to 7 g.) is considerably in excess of that which it was necessary to use. These excessive amounts were used before the very great potency of the catalyst was realized. The temperature at which the temperature controller was set is given in the fourth column of the table. In the case of a majority of the compounds hydrogenation was so rapid and the reaction so exothermic that the temperature was for a few minutes as much as 15° above the recorded temperature. The time, if any, required for the hydrogenation after the contents of the bomb reached the designated temperature is given in column 5. The pressure of hydrogen during the hydrogenation was from 100 to 150 atmospheres. The yields of products given in the last column represent the amount of the indicated product when allowance was made for the mechanical losses in handling the reaction mixture. That is, a

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[2] Lazier, British Patent 301,806, June 12, 1926; Chem. ***Abstracts,*** 23, 4306 (1929). U. S. Patent 1,746,783, Feb. 11, 1930; Chem. ***Abstracts,*** 24, 1649 (1930).

TABLE I

HYDROGENATION OF VARIOUS COMPOUNDS OVER "COPPER CHROMITE"

Compound	Moles	Catalyst, g	Temp., °C.	Time, hrs	Product(s)	Yields, %
Acetone	1.73	1	150	0.7	Propanol-2	100
Pinacolone	2.05	5	150	1 3	2,2-Dimethylbutanol-3	100
Acetoacetic ester	0.77	4	175	0.3	Ethyl β-hydroxybutyrate	77
Acetoacetic ester	.38	1	150	3.0	Ethyl β-hydroxybutyrate	100
Ethyl a-methyl-8-ketovalerate	.18	1	175	2.0	Ethyl α-methyl-β-hydroxyvalerate	100
2-Methyl-2-hydroxy-pentanone-4	41	3	160	0.1	2-Methyl-pentanediol-2,4	100
2-Methylpentanone-4	.39	1	150	2.5	2-Methylpentanol-4	100
Δ^2,2-Methylpentanone-4	.51	2	175	7	2-Methylpentanol-4	100
Benzophenone	.27	7	175	1.0	Diphenylmethane	100
Benzoin	.18	1	175	2.0	Diphenylethane	100
Acetophenone	.42	1	150	0.5	Methylphenylcarbinol	100
Benzalacetone	.14	1	175	0.2	4-Phenylbutanol-2	100
Benzaldehyde	.71	7	180	0.0	Benzyl alcohol	92
Furfural	.78	3	150	2.0	Furfuryl alcohol	100
Furfuryl alcohol	.83	3	175	11 5	Pentanediols-1,2 and -1,5	70
Nitrobenzene	.61	3	175	0 7	Aniline	100
m-Dinitrobenzene	.21	1	175	1.0	*m*-Phenylenediamine	70
Quinoline	.39	5	190	0.0	Tetrahydroquinoline	100
Pyridine	.63	5	220	9.0	Piperidine	50
Cinnamic acid	.24	2	175	0.3	β-Phenylpropionic acid	100
Cyclohexene	.50	3	165	0 0	Cyclohexane	100
N-Benzalaniline	.47	2	175	0.4	Phenylbenzylamine	100

100% yield means that no other product was formed in detectable amounts and that none of the original compound remained unhydrogenated. It has been demonstrated repeatedly that the mechanical losses can be reduced to 2% or less in this type of hydrogenation if precautions are taken to wash out the bomb, liner and filtered catalyst with a solvent.

Only five of the compounds referred to in Table I failed to give such quantitative hydrogenations. The yield of ethyl β-hydroxybutyrate was low (77%) when ethanol was not used as a solvent because of the formation of 16% of ethyl β-(β′-hydroxybutyryloxy)-butyrate and 7% of dehydroacetic acid.[3] A hydrogenation of the acetoacetic ester in ethanol resulted in a quantitative formation of the corresponding β-hydroxy ester. Eight per cent. of toluene was formed in the hydrogenation of benzaldehyde, while there were some tar-like condensation products in the hydrogenation of *m*-nitrobenzene. Pyridine was completely hydrogenated, as indicated by the amount of hydrogen absorbed, but only 50% of it was recovered as piperidine, there being an equal amount of a condensation product b. p. 143.5–147.5° (3.5 mm.). Furfuryl alcohol gave only a 70% yield of pen-

[3] *Cf.* Adkins, Connor and Cramer, THIS JOURNAL, 52, 5192 (1930).

tanediols, as there was a 10% yield of amyl alcohol along with some methyltetrahydrofuran and tetrahydrofurfuryl alcohol. The 70% yield of pentanediols was composed of 4 parts of the 1,2-glycol and 3 parts of the 1,5-glycol. Toluene, phenol, aniline, and furoic acid could not be hydrogenated under the conditions described in this paper for the hydrogenation of compounds referred to in Table I.

Discussion of Experimental Results.--Some of the characteristics of copper chromite in the catalysis of hydrogenation in the liquid phase may be described as follows. Numerous aldehydes and ketones may be quantitatively and rapidly hydrogenated to the corresponding alcohols. This holds true not only for aliphatic carbonyl compounds but also for aromatic ones, and for keto esters and a keto alcohol. A carbinol group adjacent to a benzenoid ring may be completely reduced. Nitro groups may be quantitatively converted to primary amines without the simultaneous formation of secondary amines. An alkene linkage in a hydrocarbon as well as in an acid or ketone may be hydrogenated without otherwise modifying the organic compound. Pyridinoid rings and carbon to nitrogen double bonds as in anils may be readily hydrogenated. The furanoid ring in furyl alcohol may be readily broken with the formation of 1,2- and 1,5-pentanediols in good yields. The copper chromite catalyst is not active toward cyanides or toward benzenoid nuclei and thus offers a means for the selective hydrogenation of compounds containing these groups which are so readily reducible over nickel catalysts.

The copper chromite catalyst possesses certain advantages over nickel catalysts. It is not nearly so sensitive as nickel to sulfur or halogen containing impurities in the compound to be hydrogenated. For example, the pinacolone, benzophenone, acetophenone and ethyl α-methyl-β-ketovalerate used for the hydrogenations referred to in Table I were of so poor a quality that they could not be hydrogenated over nickel. Its lesser sensitivity toward deactivation probably accounts for the fact that it is much more active after it has begun to act than is nickel despite the fact that nickel is active at lower temperatures. No special apparatus such as a reduction furnace is needed and the catalyst need not be freshly prepared before use. The catalyst ready for use does not change on standing in contact with air or moisture. In fact, it apparently need not be treated with any more care than would be accorded to such a reagent as sodium chloride. Less labor is involved in its preparation and smaller quantities may be used for reductions than is the case with the nickel catalyst. A sample of the catalyst may be used repeatedly, that is to say, it is not rapidly deactivated during use. The copper chromite catalyst is very much less active than is nickel toward carbinol groups adjacent to benzenoid rings so that it is more useful than nickel for the conversion of carbonyl groups adjacent to such a ring to the corresponding alcohol.

The rate of hydrogenation of acetone over copper chromite is very much more rapid at higher pressures. With an average pressure of 35 atmospheres the hydrogenation of 1.73 moles with 1 g. of catalyst had proceeded to the extent of only 17% in thirty minutes, while at a pressure of 148 atmospheres 60% of the acetone was hydrogenated, while at 212 atmospheres the reaction was 95% complete in the same length of time. At the end of one hour the percentage of hydrogenation was 22, 92 and 100% for the three pressures given above. The rate of hydrogenation at the lowest pressure was practically a linear function of the time.

Zinc chromite has also been used as a catalyst for hydrogenation but it is much less active than copper chromite and has been found to catalyze condensation. For example, 58 g. of acetone with zinc chromite required a temperature of 200° for a reasonable rate of hydrogenation (five and one-half hours) with 7.5 g. of catalyst and there was found almost one half as much mesityl oxide as propanol-2. Similarly, seven hours did not suffice far the complete hydrogenation of 75 g. of benzaldehyde and a condensation product, benzyl benzoate, was formed in considerable amount.

Summary

A new catalyst (copper chromite) has been tested in the hydrogenation of a group of twenty-one organic compounds in the liquid state. It has been shown to be quite superior in several respects to any catalyst hitherto used.

MADISON, WISCONSIN

[A COMMUNICATION FROM THR LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CATALYTIC HYDROGENATION OF ESTERS TO ALCOHOLS

BY HOMER ADKINS AND KARL FOLKERS

RECEIVED JANUARY 9, 1931 PUBLISHED MARCH 6, 1931

The only general method which has been used for the reduction of esters to the corresponding primary alcohols has been that involving the use of sodium and alcohol. This process was originated by Bouveault and Blanc[1] and in its various modifications has been used in the transformation of a large variety of acids, through their esters, to the corresponding primary alcohols. This reaction, however, leaves much to be desired in many cases because of low yields, difficulties of operation, and undesirable side reactions. In view of the importance of this reaction, a search for a catalyst and experimental conditions under which the reduction could be brought about by the use of hydrogen has been in progress for some time in this Laboratory. Recently this search has been successful and a method

[1] Bouveault and Blanc, *Bull. soc. chim.*, [3] 31,668 (1904).

is now available whereby various types of esters may be directly hydrogenated, as indicated in Equation 1, to the corresponding alcohols in excellent yields.

$$RCOOC_2H_5 + 2H_2 = RCH_2OH + C_2H_5OH \qquad (1)$$

The experimental methods and apparatus used in this study were the same as those previously described.[2] The catalyst, "copper chromite," was prepared as described in the preceding paper.[3]

The data on the hydrogenation of seven esters are recorded in Table I. The hydrogen pressure during the hydrogenations approximated 220 atmospheres and the temperature was 250°. The products from all the hydrogenations were subjected to fractional distillation through a Widmer column in order to separate the desired alcohol from the accompanying ethanol. In the case of ethyl valerate and ethyl cinnamate there was 1.4 and 4.5% of unreduced ester in the respective reaction mixture after hydrogenation, but in no other case was there **any** residual ester. The hydrogen absorption, as measured in each case, was from 0.03 to 0.07 mole of hydrogen above that required for the hydrogenation of the ester. This discrepancy was probably due to the diffusion of hydrogen through the walls of the bomb. The yields of alcohols given are those actually obtained, having the indicated boiling or melting point, except in the case of n-amyl alcohol, where two applications of catalyst were necessary and there was a mechanical loss. Allowance was made for the weight of product so lost in calculating the yield given in the table for this alcohol.

TABLE I

HYDROGENATION OF ESTERS

Ester		Catalyst,	Time,		
Name	Mole	g.	hrs.	Yield, %	Alcohol
Ethyl laurate	0 13	3	1 8	97 5	Lauryl (m. p. 24°)
Ethyl myristate	15	5	2 0	98 5	Myristyl (m. p. 37.5–38°)
Ethyl valerate	27	5	13 0	(94 1)	*n*-Amyl (b. p. 135–136.5°)
Ethyl cinnamate	.21	3	9	83 1	Phenylpropyl (b. p. 111–12, 8 mm.)
Ethyl trimethylacetate	23	5	1 5	88 3	*Tert.*-butylcarbinol (b. p. 111–111 5, 738 mm.)
Ethyl succinate	44	7	6 5	80 5	Tetramethyleneglycol (b. p. 106, 3 5 mm.)
Ethyl 2,2-dimethyl-3-hydroxybutyrate	.21	4	0.1	98.0	Isobutyl (b. p. 106–107.5°)

It seems unnecessary to add anything to the results given in the table for the seven esters except to point out that ethyl 2,2-dimethyl-3-hydroxybutyrate during hydrogenation underwent cleavage between the 2 and 3

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[2] Adkins and Cramer, THIS JOURNAL, 52, 4349 (1930).

[3] Adkins and Connor, *ibid.*, 53, 1091 (1931).

carbon atoms with the formation of two molecules of ethyl and one molecule of isobutyl alcohol as shown in Equation 2.

$$CH_3CHOHC(CH_3)_2COOC_2H_5 + 3H_2 = 2CH_3CH_2OH + (CH_3)_2CHCH_2OH \qquad (2)$$

Unsuccessful attempts were made to hydrogenate malonic and phenylacetic esters. Both of these esters reduced the catalyst so that it was inactive for the hydrogenation of esters. It is hoped that work now in progress will make it feasible to reduce such esters.

Other catalysts for the hydrogenation of esters have been used in this Laboratory but none of them have proved as effective as copper chromite. For example, the nickel catalyst obtained by reducing nickel chromite catalyzed the hydrogenation of ethyl laurate to the extent of only 40% after seven hours at 250°.

Summary

Ethyl laurate, myristate, valerate, cinnamate, trimethylacetate and succinate have been hydrogenated over a copper chromite catalyst with the formation of the corresponding alcohols in yields of from 80 to 98%. The carbethoxy group in 2,2-dimethyl-3-hydroxybutyrate was hydrogenated to a carbinol group, and in addition the molecule underwent cleavage between the 2 and **3** carbon atoms.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 651]

STUDIES ON a-CAMPHOR DERIVATIVES. II. THE IDENTITY OF DIHYDRO-TERESANTALIC ACID WITH 7-π-APOCAMPHAN-CARBOXYLIC ACID

BY TORSTEN HASSELSTRÖM

RECEIVED JANUARY 9, 1931 PUBLISHED MARCH 6, 1931

In a previous paper the complete synthesis of 7-T-apocamphancarboxylic acid has been reported.[1] The present investigation was undertaken in order to prove the identity of this acid with dihydro-teresantalic acid. The preparation of dihydro-teresantalic acid itself was accomplished by new methods which furnish further evidence of the structure of the π-camphor derivatives.

By adding hydrogen chloride to teresantalic acid the trimethylene ring is opened and chlorodihydro-teresantalic acid formed.[2] This action of hydrogen chloride, however, does not yield a homogeneous product.[3] Rupe and Tomi[4] have investigated the action of hydrogen chloride on the methyl ester of teresantalic acid and found that two different chlorodi-

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[1] Hasselstrom, *Ann. **Acad.** Fenn., 30, 12* (1929).

[2] Muller, ***Arch.** Pharm.,* 238, 366 (1900).

[3] Semmler and Bartelt, *Ber., 40,* 3140 (1907).

[4] Rupe and Tomi, *ibid.,* 49, 2563 (1916).

hydro-teresantalic methyl esters were formed; namely, a labile liquid form which easily split off hydrogen chloride, and a more stable solid form which could be distilled without decomposition. The removal of hydrogen chloride from both forms gives the methyl ester of iso-teresantalic acid. Thus iso-teresantalic acid and teresantalic acid are stereoisomeric compounds.

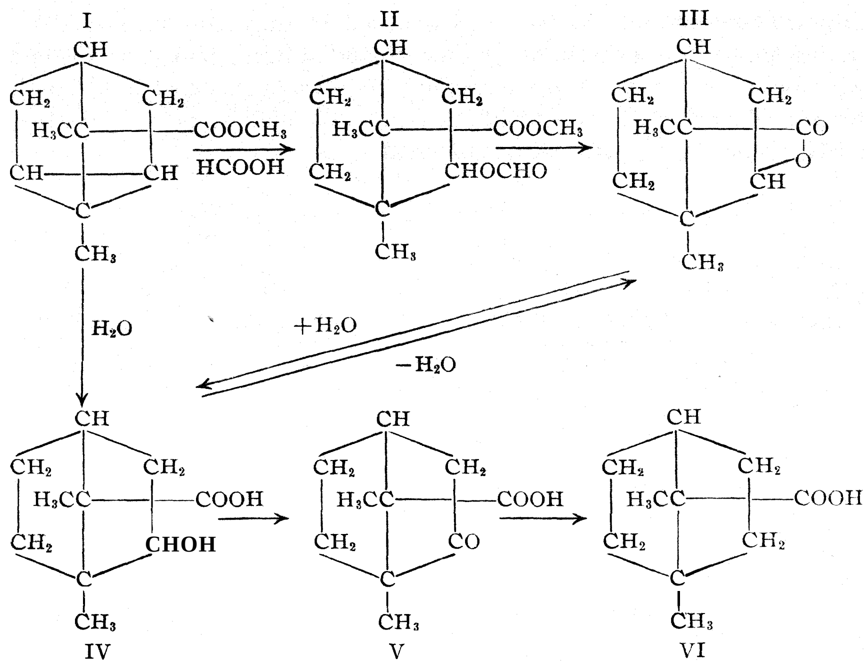
By the action of dilute alkali on chlorodihydro-teresantalic acid, Muller[2] obtained a lactone, which Semmler and Bartelt[5] later converted into the corresponding hydroxy acid and glycol. The action of formic acid on teresantalic acid results in the partial formation of a lactone, which is not identical with Muller's previously prepared lactone. Semmler and Bartelt explained the formation of their lactone by the addition and splitting off of formic acid and suggested that the lactone formed does not have the carboxyl group located in the bridge but in the ring. In order to obtain further data on this lactone formation, the preparation of dihydro-teresantalic acid was first accomplished from Semmler and Bartelt's lactone.

The teresantalic methyl ester (I) was used as starting material, instead of the free acid. This was done in order to prevent, if possible, the formation of the formate of π-norborneol. This reaction resulted in a good yield of the lactone of 2-hydroxy-7-n-apocamphan-carboxylic acid (111), from which the hydroxy acid (IV) was 'prepared by saponification with alkali. The melting points of the lactone and the hydroxy acid corresponded with those given by Semmler and Bartelt.[5] By oxidation with potassium permanganate in alkaline solution an optically active keto acid (V) was obtained, the semicarbazone of which, when treated according to the method of Wolff,[6] gave a good yield of nearly optically inactive dihydro-teresantalic acid (VI). Furthermore, the dihydro-teresantalic acid had the same melting point as the synthetically prepared 7-s-apocamphan-carboxylic acid[1] and did not give a depression by the mixed melting point test. Thus this reaction completes the synthesis of a dihydro-teresantalic acid which is identical with 7-s-apocamphan-carboxylic acid.

The action of formic acid on the methyl ester of teresantalic acid shows that the trimethylene ring is split without a rearrangement of the symmetric system and also that the carboxyl group remains in the bridge Whether or not an intermediate formate of dihydro-teresantalic methyl ester (II) is formed during this reaction was not evident. The splitting of the trimethylene ring might perhaps take place by the addition of water according to the well-known reaction of Bertram and Walbaum. The saponification of the ester group might be a secondary reaction of saponification and therefore the formation of the lactone would be due to the primary hydroxy acid (IV).

[5] Semmler and Bartelt, *Ber.*, **40**, 4465 **(1907)**

[6] Wolff, *Ann.*, **394**, *86* **(1912).**



There still remains the question of the difference between the Semmler–Bartelt and the Muller lactones. The reaction of dilute alkali on chloro-dihydro-teresantalic acid might, during the splitting of hydrogen chloride, cause a rearrangement The lactone of Muller might here react as an intermediate product in the conversion of the teresantalic series into the santene series, since the formation of lactone, thus obtained, is accompanied by more or less santene.[2] This explanation would agree with the hypothesis that the rearrangements in the true camphor series are due to an intramolecular tertiary mobile halogen or hydroxyl atom.[7] Further investigations of Muller's lactone will be necessary to provide more evidence.

Additional work was carried out on the preparation of dihydro-teresantalic acid. The crude mixture of chlorodihydro-teresantalic methyl ester (VII) was reduced to dihydro-teresantalol (VIII). This reaction was carried out with aluminum amalgam in moist ether solution at room temperature, in order to prevent the splitting off of hydrogen chloride, which readily occurs according to Rupe and Tomi.[4] As the isolated product contained chlorine, the reduction was continued by the method of Bouveault and Blanc, by means of metallic sodium and alcohol. The

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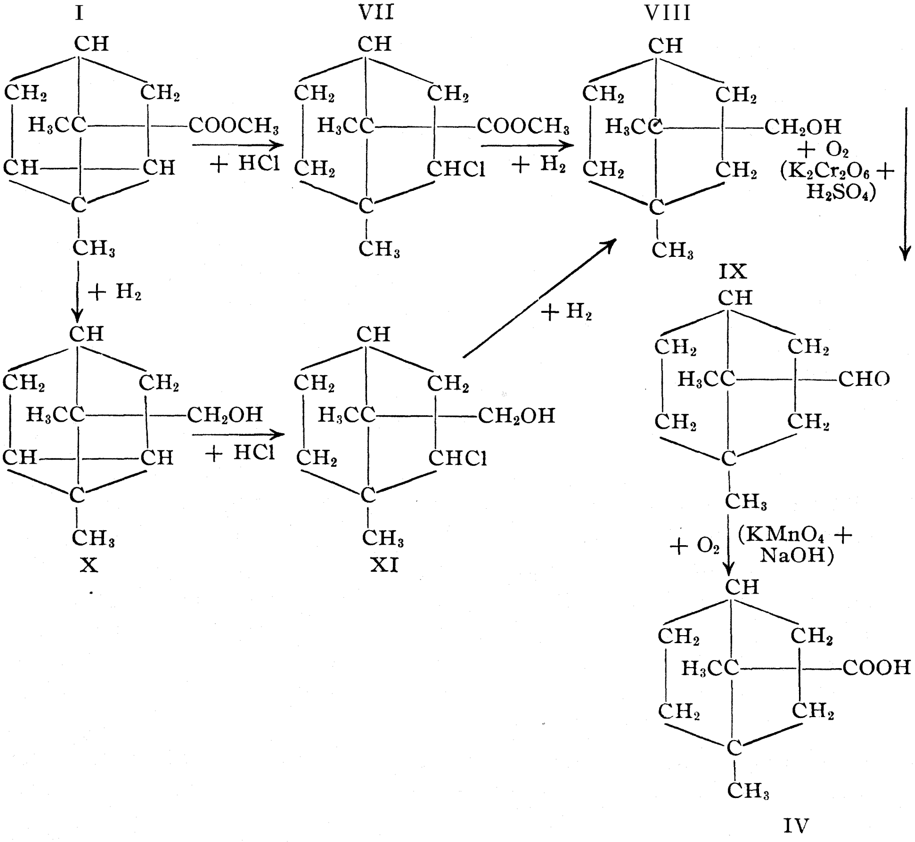
[7] (a) Meerwein and van Emster, Ber., 53, 1815 (1920); *ibid.*, 55, 2500 (1922); (b) Hasselstrbm, Ann. Acad. Fenn., 20, 2 (1923); (c) Komppa and Hasselstrom, *ibid.* 24, 14, *(d)* 15 (1925); (e) 26, 2, (f) 13 (1926); (g) 30, 13 (1929).

dihydro-teresantalol obtained was oxidized to dihydro-teresantalal (IX) with a mixture of potassium dichromate and sulfuric acid. By oxidation with potassium permanganate this aldehyde was converted into dihydro-teresantalic acid (VI), which did not depress the melting point of the previously prepared dihydro-teresantalic acid.



In order to obtain a more convenient method for the preparation of dihydro-teresantalic acid, the methyl ester of teresantalic acid was reduced to teresantalol (X) and the chlorodihydro-teresantalol (XI) obtained by the addition of hydrogen chloride was reduced to dihydro-teresantalol (VIII). However, the addition of hydrogen chloride to teresantalol seems to be accompanied by side reactions, since a solid and a liquid form of chlorodihydro-teresantalol were obtained. Further investigations of the liquid chloride, to determine whether or not a rearrangement to the santene type had taken place, were not made. The solid form of chlorodihydro-teresantalol was reduced by sodium and alcohol to dihydro-teresantalol.

The complete synthesis of dihydro-teresantalic acid, combined with the work of Ruzicka and Liebl,[8] completes the evidence for the structure of teresantalic acid.

These investigations on the a-camphor series will be continued.

Experimental

Raw Material.—The teresantalic acid was obtained from Schimmel and Co. by the courtesy of Fritzsche Bros., New York City. The purification was carried out by crystallizing the crude acid once from dilute acetic acid. The melting point was 156–157°, which corresponds with the data obtained by previous investigators.

Semmler and Bartelt's **Lactone: Lactone** of 2-Hydroxy-7-R-apocamphan-carboxylic Acid.—The methyl ester of teresantalic acid was prepared by the action of methyl sulfate on the sodium salts of teresantalic acid in water solution, according to the data given by Rupe and Tomi.[4]

To a solution of 30 g. of teresantalic methyl ester in 90% formic acid was added 5 cc. of water. The reaction mixture was allowed to boil under a reflux for one hour. After cooling to room temperature, the solution was poured into 500 cc. of a mixture of water and ice. During the treatment a solid mass separated. The product was filtered and dried on a porous plate: yield, 20 g, It was recrystallized from ethyl acetate and melted between 190–191°. Thus the melting point of the lactone corresponded to that given by Semmler and Bartelt.

An oil was obtained as a by-product. This is probably identical with the formate of π-norborneol. However, the amount was too small for an investigation.

Hydroxy Acid from Semmler **and** Bartelt's **Lactone (2-Hydroxy-7-T-apocamphan-**carboxylic Acid).—Two grams of Semmler and Bartelt's lactone was boiled under a reflux until dissolved with 150 cc. of **2%** sodium hydroxide solution. After cooling, the hydroxy acid was precipitated with dilute sulfuric acid. It was filtered and dried upon a porous plate. The crude acid was crystallized from ethyl acetate and melted at 195–196°. This melting point of the hydroxy acid corresponds to that given by Semmler and Bartelt.

Ketodihydro-teresantalic Acid (2-Keto-7-n-apocamphan-carboxylic Acid).—Five grams of the lactone was saponified by 100 g. of an alkaline solution containing 2% of sodium hydroxide. After dissolving, little by little, 120 cc. of permanganate solution, containing 8 g. of potassium permanganate, was added to the boiling solution. The mixture was stirred vigorously. The manganese dioxide was filtered off after the color of the permanganate had disappeared. The filtrate was evaporated on a boiling water-bath until 30 cc. of solution remained. After cooling, the mixture was made acid. The precipitate had all the properties of the original material. The filtrate was extracted repeatedly with ether and the ether solution dried with anhydrous sodium sulfate. After evaporating the ether, a pale yellow oil remained. This gradually solidified: yield, *4.3* g. The oil was dissolved in water, filtered, and gave a more insoluble hydroxy acid. By standing overnight, the keto acid crystallized in colorless plates. Repeatedly recrystallized from water, the acid melted at 269–270°.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.89; H, 7.75. Found: C, 66.10; H, 7.77. *Rotation.* $[\alpha]^{28}_{D}$ $-55°$ (0.52, $\alpha = 2.7°$, in 10% alcohol solution).

In comparison, the 2-keto-7-π-apocamphan-carboxylic acid previously prepared by complete synthesis melted at 249–250°.[1]

The semicarbazone of 2-keto-7-π-apocamphan-carboxylic acid was prepared in **the**

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[8] Ruzicka and Liebl, *Helv. Chim. Acta*, **9,** 140 (1926).

usual way. It melted at 204–205°, with decomposition, after one recrystallization from dilute alcohol.

7-π-Apocamphan-carboxylic Acid (Dihydro-teresantalic Acid).—Sodium ethylate was prepared in a bomb tube from 0.6 g. of sodium and 3 cc. of absolute alcohol. To the hot solution was added 0.5 g. of the crude semicarbazone of 2-keto-7-π-apocamphan-carboxylic acid. After closing the tube, the mixture was heated at 170–180" during fifteen hours. After cooling, the mixture was diluted with water and the dihydro-teresantalic acid precipitated by dilute sulfuric acid. The crude acid was recrystallized from dilute alcohol and melted at 228–229° (corr.). The acid was nearly optically inactive.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.35; H, 9.37.

In comparison, the dihydro-teresantalic acid obtained by complete synthesis melted at 229–230°.[1] No depression of the mixed melting point was obtained.

Dihydro-teresantalol (π-Borneol).—By the method of Rupe and Tomi,[4] teresantalic methyl ester was converted into chlorodihydro-teresantalic methyl ester. The oil obtained partly solidified on cooling, but the solid a-form was not separated from the labile liquid a-form, on the assumption that the α- and the a-forms are stereoisomeric compounds. Rupe and Tomi found that the hydrochlorides, by splitting off hydrogen chloride, gave the same iso-teresantalic acid, which easily was converted into teresantalic acid. Therefore the crude mixture of the chloro esters was used and the reduction carried out in such a way that the splitting off of hydrogen chloride from the labile a-form would be prevented as much as possible.

Aluminum amalgam was prepared from 25 g. of aluminum. To this moist aluminum amalgam was added 25 g. of chlorodihydro-teresantalic methyl ester, dissolved in 200 cc. of ether. After standing overnight, the mixture was filtered and the ether evaporated. The residue was a colorless oil, which. gave a strong chlorine reaction. The product was therefore dissolved in 250 cc. of absolute alcohol and the reduction continued with 25 g. of sodium according to the well-known method of Bouveault and Blanc. When the reaction was complete, water was added and the solution extracted with ether repeatedly. The ether solution was dried and, after evaporation, the residue was distilled, b. p. 214–216"; yield, 18 g. The crystalline alcohol, after removal of some oil, melted at 171°, which corresponded with Semmler and Bartelt's previously found figure.[3] The oily part was not further investigated.

Dihydro-teresantalal.—One gram of π-borneol dissolved in 10 *g.* of benzene was added to a solution of 1 g. of potassium dichromate, 1.1 g. of sulfuric acid and 10 cc. of water. The mixture was shaken and heated on a boiling water bath until the liquid became green. After cooling, the benzene layer was separated, dried, and the benzene evaporated. The residue gave a positive test for aldehyde with ammoniacal silver solution. The aldehyde was treated with semicarbazide mixture. The semicarbazone obtained was recrystallized from dilute alcohol and melted at 212–213° with decomposition.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.16; H, 9.14. Found: C, 63.23, H, 8.9.

The aldehyde, recovered by adding dilute hydrogen chloride to the semicarbazone and distilling the mixture with steam, melted at 166.5–167.5°.

Dihydro-teresantalic Acid from Dihydro-teresantalal.—Six grams of dihydro-teresantalal was oxidized at room temperature with 9 g. of potassium permanganate and 6 g. of sodium hydroxide dissolved in 200 cc. of water. The mixture was shaken for twelve hours and the reaction mixture then decolorized with alcohol. The manganese dioxide was filtered off and the filtrate evaporated to about 50 cc. The dihydro-teresantalic acid was precipitated with dilute sulfuric acid and recrystallized from dilute alcohol;

m. p. 229–230°, and no melting point depression when mixed with the previously prepared acid; yield, 4.2 g. The acid was nearly optically inactive.

Chlorodihydro-teresantalol.—Two grams of teresantalol (m. p. 114°), prepared according to Semmler and Bartelt,[3,8] was dissolved in methyl alcohol and the solution saturated with dry hydrogen chloride. The reaction mixture was cooled with a mixture of ice and salt. After standing for forty-eight hours, the mixture was poured on ice and extracted with ether. The ether solution was washed with water and a dilute sodium bicarbonate solution. After evaporation of the ether, a crystalline compound and an oil were obtained. However, the liquid part was formed in such small quantity that its further investigation was impossible. The solid part, 2-chloro-7-a-borneol melted as crude at 125–126° with decomposition.

Dihydro-teresantalol.—Two grams of 2-chloro-7-T-borne was dissolved in 30 cc. of absolute ethyl alcohol and reduced with 5 g. of metallic sodium. The reaction mixture was diluted with water and extracted with ether. After evaporating the ether, dihydro-teresantalol was obtained, m. p. 171°, and did not give any melting point depression when mixed with the previously prepared dihydro-teresantalol.

The semicarbazone of dihydro-teresantalal prepared from dihydro-teresantalol obtained by oxidation of 7-T-borneol melted at 213–214° with decomposition, thus corresponding with the previously found melting point.

Summary

1. It is proved that dihydro-teresantalic acid is identical with 7-π-apocamphan-carboxylic acid.

2. The action of formic acid on teresantalic methyl ester results in a lactone which has the carboxyl group in the ring and not in the bridge.

3. The reactions of teresantal derivatives seem to be accompanied by side reactions, which may be due either to the formation of stereoisomeric compounds or to a rearrangement of the teresantal nucleus to the santene series.

4. The complete synthesis of dihydro-teresantalic acid completes the evidence for the structure of teresantalic acid.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

AN ATTEMPTED SYNTHESIS OF A TRICYCLIC SYSTEM PRESENT IN MORPHINE

BY RICHARD H. MANSKE[1]

RECEIVED JANUARY 12, 1931 PUBLISHED MARCH 6, 1931

The intricate sociological and political problems as well as the chemical aspects serve to give to morphine a position that is unique among organic compounds. With the collaboration of the Committee on the Study of Drug Addiction sponsored by the Rockefeller Foundation the author undertook the investigation of some synthetic methods which might possibly lead to a synthesis of at least a portion of the morphine skeleton. It may be stated at once that the projected program was not completed, but the results are now recorded because the author is temporarily engaged in other problems.

In view of the complex structure of morphine, any attempt at a final synthesis is desirably preceded by a series of preliminary syntheses each devoted to only a portion of the whole molecule. The object of such procedure is to determine not only whether or not the anticipated reactions are feasible experimentally, but the optimum conditions for each stage in the process. There are three homocyclic and two heterocyclic systems in the molecule, one of these containing a nitrogen bridge. Naturally occurring examples of the latter are rare, and are in general difficult to synthesize, and although the homocyclic systems present difficulties, it was felt that the crux of the synthesis lay in the availability of the nitrogen ring system.

It has been the object of the present work to synthesize the simplest example of such a structure, and the adjoining example (I) was chosen with this in mind, especially in view of the fact that a portion of the Robinson morphine structure is here represented.[2,3] Two possible syntheses suggested themselves and the preliminary stages were conveniently carried on concurrently, especially in view of the fact that the now readily available ethyl α-cyano-β-phenylacrylate is the obvious starting point in both procedures.

In the one series β-phenyladipic acid was synthesized from phenylsuccinic acid by the well-known stages involving the reduction of the ester to the glycol, converting this first into the dibromide, then into the dicyanide and ultimately hydrolyzing the latter. The yields in several of the stages were excessively poor so that the small amount of 1-keto-1,2,3,4-tetrahydronaphthalene-4-acetic acid (II) ultimately obtained by

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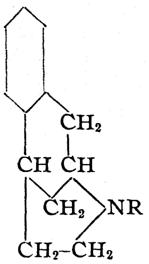
[1] Sterling Research Fellow, 1929–1930. Yale University.

[2] Cahn and Robinson, *J. Chem. Soc.*, **909** (1926).

[3] It is of considerable interest that the alkaloids of *Sinomenium* acutum, and particularly sinomenine, have been assigned consitutions closely related to morphine by Goto and by Kondo and their collaborators, *cf.*, *e.* g., *Ann.*, 470, 224 (1929).

ring closure of the acyl chloride with aluminum chloride was neither sufficient for further syntheses nor was it obtained in a satisfactory state of purity. In view of the fact that a small quantity of a tricyclic diketone (IV) was isolated from the Friedel–Crafts reaction product, it is almost certain that the acidic fraction is a mixture of the two possible keto acids, although von Braun, Bayer and Cassel[4] in an analogous case succeeded in isolating only the six-membered ring compound.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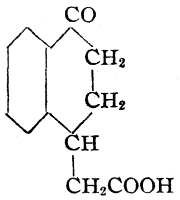
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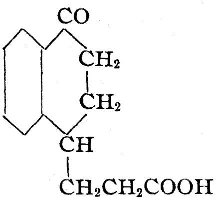
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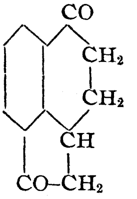
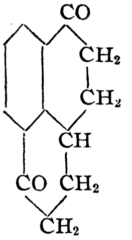

IV


V

In the second series the synthesis of γ-phenylpimelic acid from β-phenylglutaric acid by an analogous series of reactions proceeded somewhat more satisfactorily although much remains to be desired in the matter of yields. Furthermore, ring closure by means of the Friedel–Crafts reaction proceeded smoothly enough and purification of the resulting product, namely, 1-keto-1,2,3,4-tetrahydronaphthalene-4-propionic acid (III) presented no difficulties. There can be no question in this case of ambiguity of structure, a statement which also applies to the synthesis of hydrind-1-one-3-acetic acid, which was inter *alia* prepared from β-phenylglutaric acid by the same general method. The easy accessibility of the latter keto acid is conducive to its further study and the author hopes to place on record such an investigation in the near future.

As in the previous case a neutral product was obtained during the Friedel–Crafts reaction, examination of which proved it to be the tricyclic diketone (V). The two examples are of some theoretical interest because of the fact that in general it is rare that two carbonyl groups will enter the benzene ring except under drastic experimental conditions.

[4] Von Braun, Bayer and Cassel, Ber., 60, 2602 (1927).

The present observations are undoubtedly due to the particularly suitable orientation of the reacting groups.

Experimental Part

Phenylsuccinic Acid.—The procedure of Baker and Lapworth[5] for the preparation of phenylsuccinic acid is somewhat inadequate when large quantities are desired. The direct addition product of hydrogen cyanide and ethyl **a-cyano-p-phenylacrylate**[6] does not always crystallize. It is therefore extracted with ether from the acidified solution, the ether solution is thoroughly washed with water and the solvent distilled, the last small amount under reduced pressure. The residual addition product from 600 g. of unsaturated ester is heated overnight on a steam cone in a 5-liter round-bottomed flask with a mixture of 1200 cc. of concentrated hydrochloric acid and 800 cc. of water and then heated under reflux until hydrolysis and decarbonylation are complete. The mixture is then evaporated over a large Bunsen burner until unpleasant bumping commences, diluted to 4 liters with hot water, treated with norit and filtered hot. The mixture is rapidly cooled with vigorous stirring and when crystallization is complete the acid is filtered off on a large Biichner funnel, washed with iced water, drained as thoroughly as possible and then washed with about 800 cc. of benzene in small portions. The latter treatment serves to remove a greenish fluorescent material which is difficult to remove otherwise. The yield is 375 to 395 g. A further 20 g. may be obtained from the mother liquor and washings but the product is difficult to purify. As thus obtained the acid was used for the preparation of the ethyl ester, esterification being quantitatively effected by an adaptation of the continuous alcohol-carbon tetrachloride process recommended by Clarke and Davis[7] for the preparation of ethyl oxalate. The pure ester is a viscous liquid boiling at 175° (16 mm.).

β-Phenylglutaric Acid.—The preparation of β-phenylglutaric acid from the addition product of ethyl sodiomalonate in absolute alcohol to ethyl α-cyano-β-phenylacrylate by hydrolysis and decarboxylation was satisfactorily accomplished only by vigorous boiling with 48% hydrobromic acid.[8] The use of concentrated hydrochloric acid and of sulfuric acid of various concentrations was never satisfactory. In the former case boiling for ten days did not effect complete hydrolysis. **A** typical preparation is the following. A solution of 5 g. of sodium in 150 cc. of absolute[9] alcohol is treated with 170 g. of dry

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[5] Baker and Lapworth, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 88.

[6] α-Cyano-β-phenylacrylic acid may be esterified in 90% yield as follows. The acid (**346** g.), absolute alcohol (690 cc.) and sulfuric acid (45 cc.) are heated under reflux for eleven to twelve hours (optimum yield). The mixture is cooled in ice, and the crystalline ester filtered off and washed with cold alcohol (290–300 g.). The mother liquor is evaporated somewhat and yields a second crop (100–110 g.) of less pure product, but sufficiently pure for the preparation of phenylsuccinic acid.

[7] Clarke and Davis, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1922, Vol. II, p. **23.**

[8] Avery and Bouton, ***Am. Chem.* J.,*20,*** 510 (1898).

[9] Smith, **J. *Chem.*** *Soc.,* 1288 **(1927),** has provided a general technique which suffices to remove the last traces of water from commercial "absolute" alcohol when the most exacting requirements are to be met. Instead of ethyl succinate, the less expensive ethyl phthalate (27.5 g.) is added to a liter of "absolute" alcohol in which 7 g. of sodium has been dissolved. The mixture is heated under reflux for about an hour and then distilled, taking precautions to exclude atmospheric moisture throughout the entire procedure.

ethyl malonate. The still warm mixture is treated with 200 g. of **ethyl-α-cyano-β-**phenylacrylate (dried in a vacuum desiccator) in one portion, heated gently under reflux for twenty minutes, cooled, acidified to Congo red and the addition product extracted with ether and thoroughly washed with water. (It has been noted repeatedly that about 16 to 21% of the theoretical quantity of sodium is amply sufficient and in fact the yield is always better than if a whole mole be used. It may also be pointed out that ethyl cyanoacetate seems to add to the unsaturated ester with equal facility but the resultant ester is much more resistant to hydrolysis, presumably because of the consumption of a mole of acid during the hydrolysis of the additional cyano group) The oily addition product freed as far as possible from ether is heated with 360 cc. of 48% hydrobromic acid (a larger proportion of 40% acid is not as satisfactory and requires longer boiling) gently at first and vigorously after about an hour. Hydrolysis is generally complete in twenty-four to thirty hours. The mixture is diluted to one liter with hot water, boiled for some time with a generous portion of norite, filtered and cooled. The acid is filtered off, washed with cold water and with benzene (yield, 170–180 g.). Further purification*" by recrystallization from water is tedious and never yields an acid in compact well-formed crystals. However, if it is dissolved in one and one-half times its volume of boiling ethyl acetate and while still hot treated with an equal weight of benzene, slow cooling yields hard stout glistening prisms melting sharply at 140–141°[10] The recovery is well over 80%, and in the preparation of large quantities the yield of pure acid varies between 75 and 85% when the various mother liquors are worked over.

Continuous esterification by means of alcohol–carbon tetrachloride yields the pure ethyl ester quantitatively as a colorless semi-viscous liquid boiling at 188° (18 mm.).

2-Phenylbutane-1,4-diol.—Seventy grams of sodium is introduced into a 3-liter round-bottomed flask immersed in cold water, fitted with a stirrer, reflux condenser protected by a drying tube, and a dropping funnel. A solution of 62.5 g. of ethyl phenylsuccinate in 800 cc. of absolute alcohol[9] is added at the maximum rate just so that the reaction does not get out of control. When all has been added and the vigor of the reaction has subsided somewhat, the cooling water is gradually heated to boiling and the stirrer is started. In the course of about two hours the sodium has dissolved. The mixture is treated with 400 cc. of water and 800 cc. of solvent is distilled off through a short column. The remaining small amount of alcohol is removed at a water pump and the glycol then extracted from the cooled residue with a mixture of equal quantities of ether and benzene. Three successive extractions with liberal quantities of solvent suffice and when a series of runs are made the volume of solvent can be greatly reduced by using the later extracts from one run for the first extraction of the next. The solvent from the combined and cautiously washed extracts is distilled off and the residue distilled. The crude glycol is collected at 150–180° (4 mm.) and the yield from 625 g. of ester is 210 to 220 g. As thus prepared it has been used for the subsequent preparation of the dibromide. Redistillation through a short column yields a viscous colorless oil of faint but pleasant odor reminiscent of rose, b. p. 165" (4 mm.). Attempts to obtain the glycol crystalline failed. On chilling, it set to a solid glass at −10°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.61; H, 8.39.

A characteristic derivative is the *bis-phenylurethan* obtained in the usual way. After two recrystallizations from alcohol, in which it is sparingly soluble when cold, it melted sharply at 113°.

Anal. Calcd. for $C_{24}H_{24}O_4N_2$: N, 6.93. Found: N, 7.03.

2-Phenyl-1,4-dibromobutane.—A mixture of 200 g. of the crude glycol and 100 cc. of acetic anhydride was saturated with a stream of dry hydrogen bromide. The heated

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[10] All melting points are corrected.

mixture was allowed to cool to room temperature and after twenty-four hours was again saturated with hydrogen bromide and finally heated on a steam-bath for several hours. The cooled product was copiously diluted with ether, thoroughly washed with water and with sodium bicarbonate solution, dried over calcium chloride, the solvent removed and the residue distilled under reduced pressure. The yield of a mobile heavy product boiling at 173–175° (16 mm.) varies from 275 to 295 g. The dibromide loses hydrogen bromide readily and in the course of several days turns dark and turbid. Further purification to a stable colorless product was not attempted.

β-Phenyladipic Acid.—A solution of 110 g. of sodium cyanide in 100 cc. of water and 500 cc. of alcohol was treated with 292 g. of the above dibromide and heated under reflux for twelve hours, during which time the heavy oil gradually dissolved and sodium bromide separated. The dark mixture was filtered through a layer of charcoal and the residue washed with alcohol. The alcohol in the filtrate was distilled off and the mixture extracted with ether–benzene. The solvent from the washed and dried solution was removed and the residue distilled under reduced pressure. An appreciable low-boiling fraction was discarded. The higher-boiling fraction (100 g.) was obtained at 190–200° (4 mm.) and hydrolyzed without further purification by an excess of aqueous alcoholic potassium hydroxide. Removal of the solvent, extraction of an appreciable amount of unsaponifiable product, and final acidification yielded to ether extraction a colorless oily acid which on cooling set to a semi-solid mass. Benzene was added and the colorless crystals filtered off and washed with the same solvent, in which the acid is practically insoluble; yield, 35 g. One recrystallization from ether–benzene yielded well-formed rhombic plates of β-phenyladipic acid, m. p. 146°. The acid is readily soluble in acetone, ether or alcohol, but practically insoluble even in hot water.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.86; H, 6.31. Found: C, 65.53; H, 6.28.

1-Keto-1,2,3,4-tetrahydronaphthalene-4-acetic Acid. II.—A mixture of 35 g. of β-phenyladipic acid and 100 g. of phosphorus pentachloride, which liquefied in a short time, was heated for three hours on a steam cone and then freed of volatile fractions at a water pump. The residue was diluted with 300 cc. of carbon disulfide and treated with 26 g. of anhydrous aluminum chloride in small portions. The mixture was gently warmed for fifteen minutes, then cooled and the supernatant layer of carbon disulfide decanted. The dark residue was decomposed with ice and dilute hydrochloric acid, and the reaction products extracted with ether. The ether solution was thoroughly washed with water and then the acid products were removed by shaking with several successive portions of aqueous sodium bicarbonate.

There remained in the ethereal solution a small amount of a neutral substance which was obtained as an oil on removal of the ether. In the course of several days it crystallized for the greater part. The adhering oil was largely removed on a porous plate and the still somewhat yellow resinous mass recrystallized from a large volume of petroleum ether–benzene (90:10). The substance was thus obtained in minute needles (yield, about 0.5 g.) melting at 149°. Its mode of preparation together with its physical properties and analyses show the substance to be 4,9-diketo-1,2,3,4-tetrahydroacenaphthene, IV.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.42; H, 5.38. Found: C, 77.62; H, 5.24.

The acidic products present in the sodium bicarbonate extract from the ethereal solution were recovered by acidification and extraction with ether. Attempts to obtain either the free acid or the methyl ester in a state of homogeneity were unsuccessful. In view of the isolation of the above diketone it is quite certain that there is present a mixture of the two theoretically possible isomers.

3-Phenylpentane-1,5-diol.—Using the same technique and the same molecular proportions as with the lower homolog, this glycol was obtained in a 60% yield based on the crude product distilling at 175–185° (5 mm.). Redistillation yielded a colorless viscous oil of faintly pleasant odor boiling at 174° (4 mm.).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.33; H, 8.89. Found: C, 73.44; H, 8.80.

Recrystallization of the *bis-phenylurethan,* prepared in the usual way, first from alcohol and then from benzene yielded stout well-defined prisms melting at 112–113°.

Anal. Calcd. for $C_{25}H_{26}O_4N_2$: N, 6.70. Found: N, 6.76.

3-Phenyl-1,5-dibromopentane.—Of the various procedures that were tried to convert the glycol into the dibromide, only the acetic anhydride–hydrogen bromide method gave encouraging results. Following the details given for the lower homolog, from 160 g. of the glycol there was obtained 230 g. of crude dibromide, b. p. 177–182° (16 mm.), the greater portion distilling at 180'. As thus obtained it loses hydrogen bromide readily, and in the course of several days darkens appreciably. It was characterized by conversion to *3-phenyl-1,5-diphenoxypentane,* the conversion being readily effected by heating for several hours with an excess of aqueous alcoholic sodium phenate. Removal of solvents and steam distillation to remove some volatile oily impurities yielded a viscous product which crystallized in the course of several days. After pressing out on porous tile it was twice recrystallized from benzene–petroleum ether and was thus obtained in stout prisms, m. p. 72°, sparingly soluble in alcohol.

Anal. Calcd. for $C_{23}H_{24}O_2$: C, 83.13; H, 7.23. Found: C, 82.91; H, 7.12.

It may be mentioned here that several attempts to obtain the lower homolog in an analogous way yielded only uncrystallizable oils. There appears to be a much greater tendency for the elimination of hydrogen bromide due to the greater stability of the conjugated system thus produced.

γ-Phenylpimelic Acid.—The conversion of the above dibromide to the dicyanide and subsequent hydrolysis to the acid proceeded with much better yields than in the preparation of β-phenyladipic acid. From 264 g. of the dibromide and 95 g. of sodium cyanide in aqueous alcohol there was obtained 156 g. of crude dinitrile, b. p. 200–215" (4 mm.). It was at once converted into the acid by hydrolysis with excess potassium hydroxide in dilute alcohol. Removal of the solvent and extraction of the alkaline liquid with several portions of ether to remove a small amount of unsaponified product and subsequent acidification and extraction with ether yielded, after drying and evaporation of the solvent, a colorless viscous oil which crystallized readily in contact with benzene. The yield of product, m. p. 83–84°, after filtering and washing with benzene, was 132 g. A further small amount was recovered from the mother liquor. Recrystallization from ether–benzene yielded stellate aggregates of fine needles melting at 84°. Recrystallization from water is difficult on account of the low melting point but stout prisms can be obtained in the course of several months. The acid is only very sparingly soluble in cold water and but slightly when hot.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.10; H, 6.78. Found: C, 65.89; H, 6.78.

1-Keto-1,2,3,4-tetrahydronaphthalene-4-propionic acid, 111.—Without modification this keto acid was obtained from γ-phenylpimelic acid by the procedure above outlined for the lower homolog. From 94.4 g. of the acid, 84 g. of phosphorus pentachloride, 60 g. of aluminum chloride, and 300 cc. of carbon disulfide, there was obtained 48 g. (53%) of slightly colored crystalline acid melting at 105–106°. It is readily soluble in benzene and sparingly in ether, and was easily recrystallized by cautious addition of ether to a concentrated solution in benzene. As thus obtained it consisted of large colorless plates melting sharply at 108–109°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42. Found: C, 71.54; H, 6.27.

The methyl ester was prepared in the usual way as a colorless viscous oil after distillation, but it could not be induced to crystallize.

Hexahydrobenznaphthene-α,α'-dione, V.—Corresponding to the diketo compound obtained from β-phenyladipic acid there was obtained, in the ethereal extract from the preparation of the ketonaphthalenepropionic acid, a neutral product after the removal of the acids by extraction with sodium bicarbonate solution. The dried ether solution on evaporation yielded a pale brown oil which crystallized on cooling. Filtration and cautious washing with ether, in which the compound is sparingly soluble, and recrystallization from a concentrated solution in benzene by the cautious addition of ether, gave colorless stout prisms (5 g.) which melted sharply at 111°.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 78.00; H, 6.00. Pound: C, 77.55; H, 5.82.

Characterization by the preparation of the dioxime in alkaline solution with excess hydroxylamine yielded the desired substance in minute needles from acetone, m. p. 253–254° with darkening. The dioxime is readily soluble in hot acetone but only sparingly so in hot alcohol or acetic acid.

Anal. Calcd. for $C_{13}H_{14}ON_2$: N, 12.17. Found: N, 11.55.

Hydrind-1-one-3-acetic Acid.—In the course of a preliminary investigation this compound was obtained in unsatisfactory yield by treating β-phenylglutaric anhydride[11] dissolved in nitrobenzene with finely powdered aluminum chloride. The procedure which was ultimately found to give satisfactory and consistent yields was analogous to that used in the preparation of the corresponding tetralone derivatives.

A mixture of 208 g. of β-phenylglutaric acid and 420 g. of phosphorus pentachloride was gently warmed on a steam cone until reaction was complete. The phosphorus oxychloride and excess pentachloride were removed in vacuo at 100° and the cooled residue treated with 200 cc. of carbon disulfide. The addition of 140 g. of powdered aluminum chloride in small portions induced a vigorous elimination of hydrogen chloride. When reaction was complete the carbon disulfide was removed at a water pump and the dark tarry residue decomposed with ice and hydrochloric acid. The crystalline product was filtered off, thoroughly washed with cold water, freed of neutral products by solution in sodium bicarbonate and reprecipitation (yield, 178 g.). Small quantities may be recrystallized from hot water, in which it is sparingly soluble, and it is then obtained in large colorless rhombic plates melting at 155°. Larger quantities may be recrystallized from benzene–petroleum ether.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.48; H, 5.26. Found: C, 69.43; H, 5.26.

Methyl Hydrind-1-one-3-acetate.—The crude acid (190 g.) dissolved in 700 cc. of absolute methanol was heated under reflux for fifteen hours with 15 cc. of concentrated sulfuric acid. Addition of water, extraction with ether–benzene, thorough washing, finally with aqueous sodium bicarbonate and removal of solvent, yielded a dark oil which was distilled under reduced pressure. The fraction boiling at 175–180° (18 mm.) weighed 130 g. and solidified completely on cooling. Recrystallized from benzene–petroleum ether it consisted of large rhombic plates melting sharply at 54°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.59; H, 5.88. Found: C, 69.96; H, 5.86.

Addendum

In view of the low yields that were obtained in the preparation of the phenyl-glycols it was necessary to submit the method of reduction to a thorough examination to ascertain its validity. It had been observed that the toluene method described by Marvel and Tanenbaum,[12] which

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[11] Adams and Noller, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 17.

[12] Marvel and Tanenbaum, THIS JOURNAL, 44, 2648 (1922).

gave rather good yields in the case of δ-phenoxybutyl alcohol, did not improve the yields perceptibly when applied to the preparation of the phenyl-glycols. It has indeed been found that even in the preparation of the phenoxy-alcohol yields as good as previously recorded may be obtained by reducing ethyl γ-phenoxybutyrate (104 g.) with sodium (70 g.) in large pieces and absolute alcohol (650 cc.). At first the mixture is cooled to keep the reaction under control and then heated on a steam cone to dissolve the sodium completely. No stirring whatever is necessary. The alcohol is isolated in the usual way.

In one experiment where the ester contained considerable quantities of γ-phenoxybutyronitrile there was isolated also δ-phenoxybutylamine and a solid substance remained in the distillation flask which on recrystallization from benzene consisted of colorless needles and melted sharply at 94–95°. Analysis proved it to be α-phenoxybutyr-δ-phenoxybutylamide, $C_6H_5OCH_2CH_2CH_2CONHCH_2CH_2CH_2CH_2OC_6H_5$.

Anal. Calcd. for $C_{20}H_{25}O_3N$: C, 73.40; H, 7.65; N, 4.28. Found: C, 73.40; H, 7.78; N, 4.27.

ε-Phenoxyamyl Alcohol, $C_6H_5OCH_2CH_2CH_2CH_2CH_2OH$.—Ethyl δ-phenoxyvalerate (108 g.) in alcohol (800 cc.) was reduced as above described with sodium (70 g.). The alcohol isolated in the usual way was obtained as a colorless rather viscous oil, b. p. 164–166° (17 mm.), which on cooling in ice solidified completely. At room temperature it remelted, yield, 75%. It was characterized by the preparation of the phenylurethan, which was obtained in stout prisms melting at 93–94°.[13]

In conclusion it may be pointed out that ethyl sebacate when reduced by the same molecular proportions of sodium gave 1,10-dihydroxydecane in 77% yield.

Summary

1. An attempt, thus far unsuccessful, has been made to effect the synthesis of a portion of the morphine nucleus.

2. The preparation of some intermediates, notably, β-phenyladipic and γ-phenylpimelic acids, is described.

3. Two unusual cases of the easy introduction of two carbonyl groups into the benzene ring by means of the Friedel–Crafts reaction have been discovered.

4. A note regarding the reduction of esters with sodium is appended.

NEW HAVEN, CONNECTICUT

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[13] Von Rraun, Deutsch and Schmatloch, *Ber.*, 45, 1250 (1912).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

STUDIES IN THE DIPHENYL ETHER SERIES.
II. PREPARATION AND STRUCTURE OF SOME SULFONIC ACIDS AND RELATED DERIVATIVES[1]

BY C. M. SUTER

RECEIVED JANUARY 12, 1931 PUBLISHED MARCH 6, 1931

The sulfonation of diphenyl ether and its derivatives has been very little investigated. Hoffmeister[2] found that the action of concentrated sulfuric acid on diphenyl ether gave a disulfonic acid, but the positions occupied by the acid groups were not determined. The same acid[3] had been made previously but was considered to be a derivative of diphenyl. It has recently been found[4] that aminosulfonic acid sulfonates diphenyl ether to the ammonium 4-phenoxybenzenesulfonate. A number of sulfinic acids have been used as intermediates in the preparation of phenothioxin derivatives.6 Apparently no thiol substitution products have been previously investigated.

The structure of the disulfonic acid was determined by bromination of its barium salt in water solution, the bromo-monosulfonate first formed giving upon further bromination the 4,4′-dibromodiphenyl ether of known[6] structure. Since this method of determining structures has been employed previously with sulfonic acids of certain aromatic hydrocarbons,[7] phenols,[8] and amines[9,8b] without any inconsistencies becoming evident, the two sulfo groups occupy the 4,4′-positions.

The acid obtained by monosulfonation of diphenyl ether was found to give derivatives with properties which did not correspond to those reported by Quilico[4] for the compound obtained by him. However, upon repetition of his work, the products obtained by the various sulfonation methods were found to be identical.

An attempt to prepare 4-hydroxydiphenyl ether by fusion of the sodium sulfonate with sodium hydroxide was unsuccessful, as the ether linkage is broken during the reaction.

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[1] Presented before the Organic Division of the American Chemical Society at the Cincinnati Meeting, September, 1930.

[2] Hoffmeister, *Ber.*, 3,747 (1870); *Ann.*, 159, 191 (1871).

[3] Fittig, *ibid.*, 125, 330 (1863).

[4] Quilico, *Atti accad. Lincei*, [6] 6, 512 (1927).

[5] Krishna, J. *Chem. Soc.*, 123, 2782 (1923).

[6] LeFèvre, Saunders and Turner *ibid.*, 1168 (1927).

[7] Kelbe, *Ann.*, 210, 49 (1881); *Ber.*, 15, 39 (1882); Kelbe and Pathe, *ibid.*, 19, 1546 (1886); Kelbe and Koschnitzky, *ibid.*, 19, 1730 (1886); Kelbe and Stein, *ibid.*, 19, 2137 (1886); Baur, *ibid.*, 27,1619 (1894).

[8] (a) Datta, THIS JOURNAL, 41, 2028 (1919); (b) Datta and Bhoumik, *ibid.*, 43, 303 (1921); (c) Sakellarios, *Ber.*, 55, 2846 (1922).

[9] Limpricht, *Ann.*, 181, 193 (1876); Blanksma, *Rec. trav. chim.*, 29, 377 (1910); Sudborough and Lakhumalani, J. *Chem. Soc.*, 111, 41 (1910).

Bromination of sodium 4-phenoxybenzenesulfonate might conceivably result either in replacement of the sulfo group or substitution in the second benzene ring. Actually the latter takes place to the apparent exclusion of the former, as no 4-bromodiphenyl ether was found. A small amount of 4,4′-dibromodiphenyl ether was formed due to the further reaction with bromine of the bromosulfonic acid which is the primary product. Since this acid is also formed by sulfonation of 4-bromodiphenyl ether, the position of the bromine is evident. Its sodium and ammonium salts are only slightly soluble in water, as little as 12 mg. of sodium or ammonium ion in 10 cc. of solution giving a heavy crystalline precipitate with 1 cc. of a one molar solution of the acid. As much as 50 mg. of potassium gave no precipitate under similar conditions.

The action of excess chlorosulfonic acid upon diphenyl ether gives the 4,4′-disulfonyl chloride. It is apparently not possible to make the monosulfonyl chloride in this way, further sulfonation always occurring. 4-Bromodiphenyl ether reacts to give the 4′-sulfonyl chloride under the proper conditions, an excess of chlorosulfonic acid or a temperature higher than 25 or 30° leading to further sulfonation. The structure of this sulfonyl chloride is indicated by its formation from 4-phenoxybenzenesulfonyl chloride by bromination.

The 4-phenoxybenzenesulfinic acid prepared by reduction of the corresponding sulfonyl chloride was found to be quite unstable and could not be obtained in the pure state. Titration of the freshly prepared acid required 80% of the theoretical amount of alkali, while in three days this had dropped to about 50% of that calculated. The decomposition products have not been investigated.

The 4-thioldiphenyl ether when first distilled was odorless but developed the smell of hydrogen sulfide in a few hours. This was due to the decomposition of a trace of some impurity present since after standing for six months the evolution of hydrogen sulfide had ceased and the product had practically the same melting point as at first. A water solution of its sodium salt is rapidly oxidized by the oxygen of the air, crystals of the disulfide being deposited. This is also formed by oxidation of an alcohol solution of the thiol with iodine.

The sulfur analyses were made with a Parr bomb, and nitrogen was determined by the Kjeldahl method. All temperatures are corrected unless otherwise specified.

Experimental

Bromination of Barium Phenoxybenzene-4,4′-disulfonate.—To a solution of 11.8 g. (0.025 mole) of the salt 2 in 1 liter of water at 50° was added with stirring 4 g. (0.025 mole) of bromine. When the color of the bromine had disappeared, the precipitate which contained the sulfonic acid and sulfuric acid as a mixed salt was filtered off and treated with two 500-cc. portions of 0.5 normal sodium carbonate solution. The combined filtrates upon cooling deposited the slightly soluble sodium 4-bromophenoxybenzene-4'-sulfonate as thin colorless plates. The yield was 5 g., which is 57% of the theoretical.

Anal. Calcd. for $C_{12}H_8BrO_4SNa$: S, 9.12. Found: S, 8.92, 8.90.

The p-toluidine salt was obtained as small colorless plates melting at 245–247°.

Anal. Calcd. for $C_{19}H_{18}BrNO_3S$: N, 3.21. Found: N, 3.06, 3.02.

Bromination of Sodium 4-Bromophenoxybenzene-4'-sulfonate.—A bromination similar to the above gave an 84% yield of 4,4'-dibromodiphenyl ether which melted at 55–56". By recrystallizing from petroleum ether, it was obtained as large colorless needles melting at 59–60°. The value reported in the literature[6] is 60.5".

Monosulfonation of Diphenyl Ether.—This was carried out in various ways. Sulfonation in acetic acid solution with chlorosulfonic acid or in acetic anhydride with concentrated sulfuric acid was found to be better than the direct action of concentrated sulfuric acid without a solvent because this latter method gives considerable quantities of the disulfonic acid. This occurs because the monosulfonic acid first formed is soluble in concentrated sulfuric acid and is further sulfonated before the almost insoluble diphenyl ether has all reacted.

To a mixture of 170 g. (1 mole) of diphenyl ether and 100 cc. of acetic anhydride was added gradually with shaking 69 cc. (1.2 mole) of 95% sulfuric acid. After an hour on the steam-bath, the solution was poured into 1 liter of ice water. The unchanged ether (27 g.) was filtered off and the sodium sulfonate precipitated by adding 80 g. of sodium hydroxide in 250 cc. of water. There was obtained 212 g. of the dry salt, which is 93% of the theoretical based upon the diphenyl ether actually used. This product has the same characteristics as that obtained by Quilico[4] from his sulfonation product. The p-toluidine salt was obtained from dilute methanol as colorless needles melting at 221–222°.

Anal. Calcd. for $C_{19}H_{19}NO_4S$: N, 3.92. Found: N, 3.93, 3.87.

Bromination of Sodium 4-Phenoxybenzenesulfonate.—To a solution of 27 g. (0.1 mole) of the salt in 1 liter of water at 50° was added 16 g. (0.1 mole) of bromine. Separation of a precipitate began at once. After an hour the reaction mixture was heated to boiling to dissolve all water-soluble material and the solution decanted from a small amount of oil which solidified upon cooling. This, after crystallizing from petroleum ether, gave 5 g. of 4,4'-dibromodiphenyl ether. No monobromodiphenyl ether was found. Upon cooling the water solution, there separated 19.5 g. of sodium 4-bromophenoxybenzene-4'-sulfonate.

Fusion of Sodium 4-Phenoxybenzenesulfonate with Sodium Hydroxide.—This was carried out under different conditions, none of which gave an appreciable yield of 4-hydroxydiphenyl ether. A mixture of 27 g. of the sodium salt and 100 g. of sodium hydroxide was heated at 260° for fifteen minutes and then dissolved in water. There was recovered 10 g. of unchanged sodium salt and upon acidifying with hydrochloric acid a small amount of a flocculent precipitate separated. This was too small in quantity for examination. Phenol and sodium sulfite were present in considerable amounts in the solution. A similar fusion carried out at 300° gave no products insoluble in water when the reaction products were treated like the above.

4-Phenoxybenzenesulfonyl Chloride.—Heating a mixture of 181 g. (0.66 mole) of the sodium sulfonate with 70 g. (0.33 mole) of phosphorus pentachloride under reflux at 170–180° for ten hours gave 125 g. of an oil of which upon fractionation 95 g. or 54% of the theoretical amount boiled at 205–207° (uncorr.) under 12 mm. pressure. This solidified upon cooling and crystallized from petroleum ether as colorless needles melting at 45–46°. Treatment of the sodium salt of the acid obtained by Quilico's method in the same manner gave the same sulfonyl chloride, although he reports it to be an oil.

Anal. Calcd. for $C_{12}H_9ClO_2S$: S, 11.92. Found: S, 12.09.

The amide was made by treatment of the sulfonyl chloride with a mixture of ammonium hydroxide and alcohol. It was purified by crystallizing its sodium salt from water, redissloving in water and acidifying with acetic acid. It melted at 128–129°; previously[4] reported, 88°.

Anal. Calcd. for $C_{12}H_{11}NO_3S$: N, 5.52. Found: N, 5.59, 5.79.

The anilide obtained from a mixture of the sulfonyl chloride with aniline and 10% sodium hydroxide solution melted at 86–88°.

Anal. Calcd. for $C_{18}H_{15}NO_3S$: N, 4.31. Found: N, 4.26.

Sulfonation of 4-Bromodiphenyl Ether. (a) With Sulfuric Acid.—A mixture of 25 g. (0.1 mole) of 4-bromodiphenyl ether and 11 cc. (0.2 mole) of 95% sulfuric acid was warmed on the steam-bath until it was homogeneous, poured into 400 cc. of water, and sodium hydroxide added to precipitate the sodium salt. There was obtained the theoretical yield of the 4'-sulfonate identical with that from bromination of the mono- and di-sulfonic acid salts. For precipitation tests with sodium, potassium, and ammonium ions, a reaction mixture similar to the above was diluted to 100 cc. with water and 1-cc. portions of this solution added to 10 cc. of the solution to be tested. As little as 12 mg. of sodium as sodium nitrate gave a precipitate within a few minutes, while 9 mg. gave a slight precipitate after standing for twelve hours; 10 mg. of ammonium also gave a slight precipitate after twelve hours; 100 mg. of potassium gave a precipitate within half an hour, 75 mg. after twelve hours, and 50 mg. gave no precipitate.

(b) With Chlorosulfonic Acid.—To 25 g. (0.1 mole) of 4-bromodiphenyl ether was added with shaking 15 cc. (0.22 mole) of chlorosulfonic acid. The thick oily mixture was poured into ice water and the solid acid chloride filtered off. The yield was 16 g. of product which crystallized from petroleum ether as plates melting at 81–82°. The water-soluble sulfonation products did not include the monosulfonic acid, as they gave no insoluble sodium salt.

The same sulfonyl chloride was obtained in 91% yield by bromination of 4-phenoxybenzenesulfonyl chloride in carbon tetrachloride solution.

Anal. Calcd. for $C_{12}H_8BrClO_3S$: S, 9.23. Found: S, 9.35.

The amide was obtained from dilute methanol as colorless plates melting at 131–132°.

Anal. Calcd. for $C_{12}H_{10}BrNO_3S$: N, 4.25. Found: N, 4.20.

The corresponding anilide after crystallizing from dilute methanol several times melted at 108–109°.

Anal. Calcd. for $C_{18}H_{14}BrNO_3S$: N, 3.47. Found: N, 3.52.

Phenoxybenzene-4,4'-disulfonyl Chloride.—To 85 g. (0.5 mole) of diphenyl ether was added with shaking 200 cc. of chlorosulfonic acid. After two hours the mixture was poured into 2 liters of water and the crude disulfonyl chloride filtered off. The yield was 160 g. or 88% of the theoretical of material which crystallized from petroleum (90–120°) as colorless needles melting at 128–129°.

Anal. Calcd. for $C_{12}H_8Cl_2O_5S_2$: S, 17.45. Found: S, 17.35.

The diamide crystallized from hot water, in which it is somewhat soluble, as shiny plates melting at 158–160°.

Anal. Calcd. for $C_{12}H_{12}N_2O_5S_2$: N, 8.53. Found: N, 8.56, 8.75.

4-Phenoxybenzenesulfinic Acid.—A mixture of 13.5 g. (0.05 mole) of the sulfonyl chloride, 6.5 g. (0.05 mole) of sodium sulfite, and 6 g. of sodium carbonate in 75 cc. of water was refluxed for half an hour to complete the reaction. The mixture was filtered to remove a small amount of water-insoluble material and the solution cooled. There separated 9.8 g. of colorless needles of the sodium sulfinate. This was recrystallized once from hot water.

Anal. Calcd. for $C_{12}H_9O_3SNa$: Na, 8.97. Found: Na, 8.98, 8.97.

By acidifying the filtrate after removal of the sodium sulfinate, there was obtained a chalky white precipitate which was not the sulfinic acid. When heated, it darkened above 180° with no definite melting point. Titration with standard alkali gave an equivalent weight approximately twice that of the sulfinic acid. It is planned to investigate this and similar products further.

Adding acid to a water solution of the sodium sulfinate precipitated an oil which soon solidified. After drying for several hours, a sample of this was titrated with standard alkali.

Anal. Calcd. for $C_{12}H_{10}O_3S$: 0.5049 g. requires 21.8 cc. of 0.099 *N* NaOH. Found. 17.6 cc. After standing for three days in a desiccator, another sample was titrated. 0.1973 g. requires 8.43 cc. of 0.011 *N* NaOH. Found: 4.11 cc.

Another similar sample showed a drop in melting point from 100–101° to 91–93° in forty-eight hours. Because of this instability, further attempts to obtain the acid in a pure condition were not made.

4-Thioldiphenyl Ether.—To a mixture of 70 g. of concentrated sulfuric acid and 210 g. of crushed ice was added with stirring 27 g. (0.1 mole) of the sulfonyl chloride and then 35 g. of zinc dust, the temperature being kept below 0°. After standing for two hours, the mixture was refluxed for two and one-half hours, filtered from a little unchanged zinc, and extracted with benzene. The benzene was evaporated and the residue distilled under reduced pressure. The yield was 12 g. or 60% of the theoretical of a colorless oil boiling at 178–180° at 20 mm., which solidified upon cooling and melted at 19–22". The product thus obtained always gave a low sulfur analysis even after repeated distillation. Recrystallizing from petroleum ether by cooling the solution to −10° gave colorless plates of a pure product melting at 21–22°.

Anal. Calcd. for $C_{12}H_{10}OS$: S, 15.86. Found: S, 15.67.

A sample was also titrated in alcohol solution with standard sodium hydroxide using phenolphthalein as the indicator.

Anal. Calcd. for $C_{12}H_{10}OS$: 0.2132 g. requires 10.7 cc. of 0.099 N alkali. Found: 10.5 cc.

The disulfide was formed by oxidation of a water solution of the sodium salt of the thiol by air, or by treatment of an alcoholic solution of the thiol with iodine. It crystallized from methanol as colorless plates which melted at 47–48°.

Anal. Calcd. for $C_{24}H_{18}O_2S_2$: S, 15.95. Found: S, 15.90.

Summary

The sulfonation of diphenyl ether with both sulfuric acid and chlorosulfonic acid has been studied and the structures of the products formed have been determined by replacement of the sulfo groups with bromine. In all cases, sulfonation occurs in the para positions when these are unoccupied by other groups.

The sulfinic acid and thiol have been obtained by reduction of 4-phenoxybenzenesulfonyl chloride. The sulfinic acid was found to be very unstable.

EVANSTON, ILLINOIS

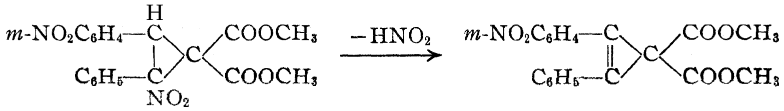
[CONTRIBUTION FROM SCIENCE HALL, LAWRENCE COLLEGE]

STUDIES IN THE CYCLOPROPENE SERIES. I. DIPHENYLCYCLOPROPENEDICARBOXYLIC ACID

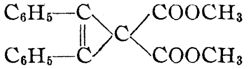
BY S. F. DARLING AND E. W. SPANAGEL

RECEIVED JANUARY 12, 1931 PUBLISHED MARCH 6, 1931

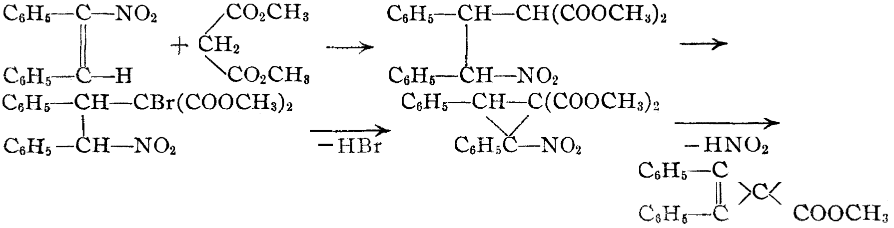
In connection with a study of the behavior of nitrocyclopropane derivatives with bases Kohler and his students[1] have postulated the presence of a substituted cyclopropene derivative intermediate between the nitrocyclopropane and the end-product. Later they actually succeeded in isolating a new type of cyclopropene derivative[2] (I) as the first product of the action of sodium methylate on the nitrocyclopropane (II). This


II I

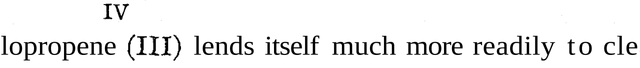
substance suggests many new problems for study but the presence of the nitro group in one of the benzene nuclei is undesirable in certain cases. We have therefore prepared another cyclopropene derivative (III) differing


III

from the cyclopropene (I) in that both phenyl groups are unsubstituted. The reactions which lead to this substance are as follows



The proof of the structure of this new cyclopropene derivative is analogous to the proof of the constitution of (I). The corresponding dibasic acid (IV) on oxidation with potassium permanganate in alkaline solution forms dibenzoylmethane. Therefore we may write the following reaction


IV

The cyclopropene (III) lends itself much more readily to clean cut reactions than the cyclopropene derivative (I); however, its preparation

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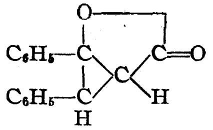
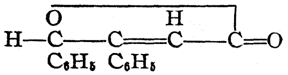
[1] Kohler, THIS JOURNAL, 44, 624 (1922).

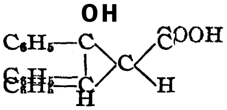
[2] Kohler, *ibid.*, 52, 1174 (1930).

entails many difficulties and low yields result. The work described in this paper is confined to the study of the effect of heat on the dibasic acid (IV). This compound melts to a clear, pale yellow liquid at about 190°, with the evolution of carbon dioxide. If this clear melt after cooling is manipulated with appropriate solvents a good yield of a new substance whose composition corresponds to the loss of one molecule of carbon dioxide from the dibasic acid, is obtained. Contrary to our expectations this substance proved to be a lactone instead of a mono basic acid. A little reflection about the matter shows that two formulas for this lactone are probable; the cyclic lactone (V) and the corresponding open-chain unsaturated lactone (VI).


V


VI

In order to assign the more probable formula to this lactone we have converted it into the corresponding hydroxy acid and subjected this substance to ozonization. There is little doubt that the hydroxy acid derivable from a substance of formula (VI) would form benzoin as one of the products of ozonization. Benzoin could easily be isolated and identified. The hydroxy acid related to a substance of formula (V) should resist ozonization or at most undergo a little general oxidation. The hydroxy acid remained almost totally unchanged in the presence of a moderate stream of ozone and over 75% of the material was recovered unchanged after being subjected to a rapid stream of 6% ozone for three hours. Little doubt therefore remains that the lactone should be represented by formula (V) and the hydroxy acid by formula (VII). Substances of this type are practically unknown; in fact previous attempts to introduce hydroxyl groups in the cyclopropane ring have led to open-chain compounds. We hope that additional work with cyclopropene derivatives will further characterize this little-known class of compounds.


VII

Experimental Part

The a-Bromo Compound Formed by Indirect Bromination.—Ten grams of dimethyl β,γ-diphenyl-γ-nitro-ethyl-malonate, prepared according to the method of Kohler and Barrett,[3] was suspended in 30 cc. of dry methyl alcohol and to this was added 1.3 *g*. of sodium as sodium methylate. This caused the substance to dissolve and to form a light yellow solution. This solution was cooled and poured slowly into a cold solution of excess bromine in 25 cc. of *dry* methyl alcohol. The crystals of bromine compound separated promptly and were purified by crystallization from methyl alcohol, from which solvent they separate in stout, colorless crystals which melt at 117–118°. The yields vary between 70 and 80% of the theoretical.

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[3] Kohler and Barrett, THIS JOURNAL, 48, 1770 (1926).

Dimethyl α-Bromo-β,γ-diphenyl-γ-nitro-ethyl-malonate.—This substance is isomeric with the bromine compound prepared by Kohler and Barrett[3] by direct bromination of the nitro ester.

Anal. Calcd. for $C_{19}H_{18}O_6NBr$: C, 52.3; H, 4.1. Found: C, 52.1; H, 4.2.

Preparation of the Nitrocyclopropane.—Thirty grams of the above bromine compound was pulverized and added to a solution of 30 g. of potassium acetate in 250 cc. of dry methyl alcohol. The mixture was refluxed for thirty minutes, during which time the substance dissolved, the solution developed a yellow color, and potassium bromide separated. The solution was cooled and to it was added enough water to dissolve the potassium bromide. After standing for several hours the solution deposited 6–7 *g.* of pure nitrocyclopropane derivative, which melted at 129°. The mother liquor was removed by decantation and after further standing it deposited the isoxazoline oxide, melting point 140°, previously described by Kohler and Barrett.[3] After removal of the oxide the solution sometimes deposited a crop of unchanged isomeric bromine compound when the crude bromine compound was used instead of the pure substance melting at 117–118°.

Dimethyl 1,2-Diphenyl-2′-nitro-3,3′-cyclopropane Dicarboxylate.—This substance separates from methyl alcohol in large, lustrous plates which melt at 129".

Anal. Calcd. for $C_{19}H_{17}O_6N$: C, 64.2; H, 4.8. Found: C, 64.0; H, 4.8.

Preparation of the Cyclopropene Diester.—Five grams of nitrocyclopropane was dissolved in 60 cc. of hot, dry methyl alcohol and to this was added 1 g. of sodium as sodium methylate. The solution was refluxed for fifteen minutes, during which time sodium nitrite separated. In one experiment the sodium nitrite was filtered off and identified. However, in most cases water was added to the cold solution until it precipitated the cyclopropene ester. The yield is about 1–1.5 g. Some cyclopropene dibasic acid can be recovered by acidification of the mother liquors.

Dimethyl 1,2-Diphenyl-3,3′-cyclopropene Dicarboxylate.—After several crystallizations from a mixture of ether and petroleum ether the substance was pure. It separates in beautiful, colorless prisms which melt at 140–142°.

Anal. Calcd. for $C_{19}H_{16}O_4$: C, 74.0; H, 5.2. Found: C, 74.1; H, 5.5.

The Cyclopropene Dibasic Acid.—Two-tenths gram of the cyclopropene ester was refluxed for ten minutes with excess methyl alcoholic potash. The alcohol was removed and the cold solution was acidified. An oil separated which soon solidified. After purification from a mixture of ether and petroleum ether the substance separated in stout, colorless needles which melted with the evolution of carbon dioxide at about 190°.

Anal. Calcd. for $C_{17}H_{12}O_4$: C, 72.9; H, 4.3. Found: C, 73.1; H, 4.6.

Oxidation of the Dibasic Acid.—One-tenth gram of the cyclopropene dibasic acid was dissolved in excess 10% sodium carbonate solution to which was added potassium permanganate solution until the purple color persisted. The solution was cleared with sodium sulfite solution and finally acidified with dilute hydrochloric acid. The substance which separated was extracted with ether and the ethereal solution shaken with a saturated solution of copper acetate. The pale green copper compound which separated melted at 295–300° with decomposition after crystallization from benzene. The copper derivative of dibenzoylmethane melts at 294–301° with decomposition. The remainder of the copper compound was shaken with water containing a small amount of dilute acid and an ether upper layer. The ether layer after evaporation deposited a substance which melted at 75–77°. A mixed melting point with a known sample of dibenzoylmethane showed no depression.

Addition of Bromine to the Cyclopropene Diester.—Two-tenths gram of cyclopropene ester in chloroform solution absorbed bromine from a 5% solution of bromine in carbon tetrachloride in direct sunlight. The solvent was removed under diminished pressure and the oil which remained crystallized after manipulating with methyl alcohol. It separates in small, colorless crystals from methyl alcohol which melt at 194–5° with decomposition.

Dimethyl 1,2-Dibromo-1,2-diphenyl-3,3′-cyclopropane Dicarboxylate.—*Anal.* Calcd. for $C_{19}H_{16}O_4Br_2$: C, 48.7; H, 3.4. Found: C, 49.0; H, 3.4.

Decomposition of the Cyclopropene Dibasic Acid. The Lactone.—Two-tenths gram of the cyclopropene dibasic acid was melted in a Pyrex test-tube heated by means of a sulfuric acid bath and maintained at the decomposition point until the carbon dioxide was all evolved. The clear melt was cooled and then taken up in ether, from which it soon separated in colorless crystals. It melts at 149–151°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1. Found: C, 81.2; H, 5.6.

Hydrolysis of the Lactone.—Six-tenths gram of lactone was dissolved in 10 cc. of methyl alcohol to which had been added excess potassium hydroxide solution. A deep purple solution resulted which became lighter as the solution was heated on the water-bath. After removal of the methyl alcohol, which was gradually replaced by water, the clear solution was cooled and acidified. A substance separated which was crystallized from a mixture of ether and petroleum ether. It separates in small, octahedral crystals which melt at 146–148°.

1,2-Diphenyl-2-hydroxy-3-cyclopropane Carboxylic Acid.—Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.5; H, 5.5. Found: C, 75.1; H, 5.6.

Ozonization of the Hydroxy Acid.—Four-tenths gram of the hydroxy acid was ozonized cautiously in ethyl bromide for half an hour, after which almost the whole of the material was recovered unchanged. Finally another 0.4 g. was ozonized in a rapid current of 6% ozone for three hours after which more than 0.3 g. was recovered unchanged. Ozone therefore has no effect on the compound.

Summary

1. Another cyclopropene derivative has been prepared.
2. The dibasic acid obtained from this cyclopropene diester loses carbon dioxide at its decomposition point to form a cyclopropane lactone.

APPLETON, WISCONSIN

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[4] We are indebted to Professor E. P. Kohler of Harvard University who, with Dr. E. M. Nygaard, carried out this experiment for us.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND OF LEMOORE HIGH SCHOOL]

THE INDUCTION OF THE REACTION BETWEEN CHLORINE AND BENZENE BY ETHYLENE

BY T. D. STEWART AND M. H. HANSON

RECEIVED JANUARY 13, 1931 PUBLISHED MARCH 6, 1931

In the reaction between ethylene and chlorine Stewart and Smith[1] postulated a chain mechanism of the type

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2^* \xrightarrow{Cl_2} C_2H_3Cl_3 + HCl + \text{Heat} \qquad \text{(Ia)}$$

$$C_2H_4Cl_2^* \xrightarrow[\text{Wall}]{O_2} C_2H_4Cl_2 + \text{Heat} \qquad \text{(Ib)}$$

$$C_2H_4Cl_2^* \xrightarrow[Cl_2]{C_2H_4} 2C_2H_4Cl_2^* \qquad \text{(Ic)}$$

in which the starred formulas represent an intermediate compound, presumably an activated ethylene dichloride.

The experiments described here were first designed to determine whether this intermediate would induce a reaction in other reacting systems, or itself undergo a reaction with other substances (than chlorine). For instance, in the presence of benzene, a Friedel–Crafts reaction is possible between the intermediate and benzene, or in the presence of both benzene and benzoyl chloride, benzophenone might be formed. Thorough search for these reactions has shown no indication of them. Oxidations of the reaction products by alkaline permanganate or chromic acid have yielded only traces of materials which could be considered aromatic carboxylic acids. Similarly, when the reaction between ethylene and chlorine was carried out in the presence of a mixture of benzoyl chloride and benzene, no trace of benzophenone could be found.[2]

However, when benzene is used as a solvent for the chlorine-ethylene reaction, considerable benzene hexachloride is always formed, usually a mixture of the stereoisomeric forms, with the a-form (m. p. 157°) predominating.

$$C_6H_6 + 3Cl_3 \longrightarrow C_6H_6Cl_6$$

This reaction has long been known as one susceptible of induction by light,[3]

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[1] Stewart and Smith, THIS JOURNAL, 51, 3091 (1929); 52, 2869 (1930).

[2] The reaction mixture was distilled to remove ethylene dichloride and benzene, the residue completely hydrolyzed in dilute alkali, and the alkaline solution extracted with benzene. The residue from this extract, distilling above 100°, yielded no oxime soluble in dilute alkali but insoluble in neutral water solution (10 cc.).

[3] Faraday, Ann. Chem., [2] 4,472 (1825); Slator, *Z. physik. Chem.*, 45, 540 (1903). Luther and Goldberg, *ibid.*, 56, 43 (1906), state that light is necessary even in boiling benzene. They studied the inhibiting effect of oxygen, from which Alyea (Ref. 6) estimates the quantum efficiency as about seventy-five moles per quanta.

alkali,[4] iodine[6] and alpha particles.[6] The first and last of these have been shown to have a chain mechanism. The efficiency of the induction by ethylene is then of particular interest and the effect of the physical conditions of the experiments upon this efficiency of importance.

The above reaction is not the sole reaction. Considerable hydrogen chloride is often formed, indicating some substitution. In our experience phenyl chloride is not a product. When little or no hydrogen chloride is formed the product is cleanly crystalline, but otherwise it is contaminated by gummy higher chlorinated substitution products of benzene. There are thus two criteria as to the nature of the reaction itself. The substitution reaction is favored by low chlorine concentrations in the photochemical and presumably so in ethylene-induced reactions. No attempt is made here to formulate the actual products of substitution (see Equation II′c below).

A Provisional Mechanism.—The experimental results may be correlated by means of the following series of steps, in which chain mechanisms for both the ethylene–chlorine and benzene–chlorine reactions are assumed, but without precise specification of the mechanism of chain propagation.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2^* \begin{cases} \xrightarrow[\text{Wall, } O_2]{C_6H_6} C_2H_4Cl_2 + \text{Heat} & \text{IIa} \\ \xrightarrow[Cl_2]{C_2H_4} 2C_2H_4Cl_2^* \ldots\ldots \longrightarrow C_2H_4Cl_2 + \text{Heat} & \text{IIb} \\ \xrightarrow[3Cl_2]{C_6H_6} C_6H_6Cl_6^* + C_2H_4Cl_2 \xrightarrow[3Cl_2]{C_6H_6} 2C_6H_6Cl_6^* & \text{IIc} \\ C_6H_6Cl_6^* \xrightarrow[\text{Wall, } O_2]{C_6H_6} C_6H_6Cl_6 + \text{Heat} & \text{IId} \end{cases}$$

Reaction IIc might better be written as follows

$$C_2H_4Cl_2^* \xrightarrow[Cl_2]{C_6H_6} C_6H_6Cl_2^* + C_2H_4Cl_2 \xrightarrow{Cl_2} C_6H_6Cl_4^* \begin{cases} \xrightarrow{Cl_2} C_6H_6Cl_6^* \ldots\ldots & \\ \xrightarrow{-HCl} C_6H_5Cl_3(?) + \text{Heat} & \text{II}'\text{c} \end{cases}$$

Other possibilities present themselves, such as reaction Ia, but in numerous fractional distillations, no fractions corresponding to the tri- and tetrachloroethanes have been observed. This reaction is believed to

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[4] Matthews, Trans. *Chem. Soc.*, 59, 166 (1891). Luther and Goldberg (Ref. 3, p. 55) state that alkali serves as a catalyst even with the total exclusion of light.

[5] Müller, J. *Chem. Soc.*, **15**, 41 (1862), states that the use of iodine as a catalyst results largely in substitution products.

[6] Alyea, THIS JOURNAL, 52, 2743 (1930).

have been inhibited by the benzene. Another type reaction, suggested to us by Professor G. N. Lewis, presumes no ethylene dichloride formed.

$$C_2H_4Cl_2^* + C_6H_6 + 2Cl_2 \longrightarrow C_6H_6Cl_6^* + C_2H_4 \ldots.$$

We have not observed conditions wherein little or no ethylene is used up. Moreover, when ethylene and chlorine react in the presence of ethylene dichloride (no benzene), the course of the substitution reaction approximates that of Equation Ia, since the hydrogen chloride produced never exceeds, in moles, the ethylene used up, which it might do if the hypothetical intermediate acted simply as a chlorinating reagent. The appearance of ethylene dichloride as an isolable product would tend to eliminate this type of mechanism as a major step in the process. The rupture of the benzene–chlorine chains by ethylene (or chlorine) is probable.

Experimental Results

The main observation was the proportion of total chlorine used up which reacted with the benzene. This was measured by weighing the non-volatile products formed and by noting the molal ratio of chlorine to ethylene reacting. This ratio would be unity if the chlorine reacted solely with the ethylene, and only by addition (see above). Any excess of chlorine used up, as shown by a value of this ratio greater than unity, is taken to mean reaction with benzene.

The Homogeneous Reaction between Ethylene and Chlorine Dissolved in Benzene.—The reagents were dissolved separately, and equal volumes of the solutions mixed and allowed to stand for two hours or more in the dark. The results were very discordant, but a few conclusions may be drawn. (1) The presence of glass wool or glass beads in the reaction mixture causes no difference in the molal ratio of total chlorine to ethylene used up, or in the nature or amount of the product. (2) This molal ratio varied from 1.7 to 2.2 when the chlorine concentration lay between 0.3 and 0.42 M and the ethylene concentration changed from 0.042 *M* (initial) to zero. In one experiment, with the chlorine within the above limits, but with the initial ethylene concentration at 0.013 M, this ratio was 10. When both were low (chlorine 0.036 M, ethylene 0.0043 M) the ratio was 1.26, very little of the chlorine reacting with benzene. (3) In all cases the amount of non-volatile residue was close to that predicted on the assumption that it consisted of benzene hexachloride and was formed from that excess of chlorine over ethylene indicated by the above ratios (little or no phenyl chloride was formed). But the product was always gummy in character, and the hydrogen chloride production was much higher than in experiments to be described later. (4) In the absence of ethylene the disappearance of chlorine is represented by the following figures.

Time (hours)	0	16	40	68
Chlorine concentrations (m./l.)				
(a) Dark	0.431	0.447	0.444	0.431
(b) Diffused light	...	.372	.346	.326
(c) Dark	.0347	.0357	.0364	.0352

These solutions were all quiet; the reaction in diffused light is enormously hastened by constant shaking, but in the dark is unaffected (Expts. 2a and 2b, Table II). The variations above suggest analytical difficulties in part. Eventually these analyses could be reproduced to 1%. There is no evidence to indicate that diffused light affects the reaction induced by ethylene, since the ethylene-induced reaction was the same (in two hours) in the dark and in diffused light.

The homogeneous reaction is then attended by an undue amount of benzene substitution even at high chlorine concentrations, and a low efficiency of induction except in one case, which suggested that the efficiency of induction might be a function of the ethylene concentration, *i. e.*, higher at lower ethylene concentrations. This would be expected on the basis of the competitive effect of Equations IIb and IIc.

Experiments with Chlorine Dissolved in Benzene and the Ethylene Introduced into the Vapor Phase. I. Bubbler Experiment.—In the first experiments dry ethylene gas was bubbled through the chlorine–benzene solution. The reaction vessel was essentially a glass tube, about 1 cm. in diameter and 25 cm. long, with smaller glass tube connections at each end. When filled with the solution and placed in a gently sloping position the bubbles of gas traveled the length of the tube, in contact with both the wall and the solution. The rate of flow varied from one to two cubic centimeters per minute, so that most of the gas entering was absorbed. The bubbles seemed to decrease to one-half or one-third their original volume, but the fraction of entering gas which was recovered was usually less than one-tenth This seemed to indicate that a large proportion of the reaction took place at the entrance and exit. The point of interest is that in these experiments the ethylene partial pressure in the gas phase was high, and varied probably from two-tenths to five-tenths of an atmosphere. Table I gives a summary of the results. The average chlorine concentration varied in the different experiments. The hydrogen chloride formed should be considered a maximum, and of significance only as indicating very little substitution, for analytical reasons (see Experimental Part). The weight of product is not consistent with the amount of chlorine and ethylene used. This also involves an analytical difficulty (see footnote, Table II) and is not considered to alter the major conclusion that this method of introducing the ethylene leads to a definite reaction between the chlorine and benzene, to the extent of about half the total reacting chlorine, with comparatively little substitution.

TABLE I

EXPERIMENTS WITH BUBBLES

Vol. of solution, 73 cc.; temp., 22–23°; semi-darkened room. Time: Expt. A, 45 min.; Expts. B, C, D, 4 hours. In Expts. A, B and C the reaction vessel was cleaned by solvents and air-dried at 100°; in Expt. D, by ignition in dry oxygen. Product was recovered as residue upon evaporation at room temperature and 3 mm. pressure.

Expt.	Concn. of Cl_2 moles/liter Initial	Final	Moles of reactants Cl_2	C_2H_4	Ratio Cl_2/C_2H_4	Moles HCl (at end)	Product, g.
A	0.425	0.313	0.00814	0.00318	2.56	0.00137	0.411
B	.853	.406	.0326	.0149	2.19	.00250	1.45
C	1.437	.978	.0335	.0152	2.20	.00715	2.36
D	1.297	.782	.0375	.0158	2.37	....	2.51

II. Shaker Experiments.—In these experiments, summarized in Table II, a large glass tube, sealed at both ends and provided with a side tube in the center, was the reaction flask. It was partly filled with the chlorine–benzene solution, connected to the ethylene supply through a three-way stopcock in the side tube, and placed on a rocker which caused the gas bubbles present to travel the length of the tube about once every second. The gas space could be varied at will and could be filled initially (by solution displacement) with ethylene, air or nitrogen. The ethylene supply was under constant pressure, and the gas flowed in as fast as the ethylene was used up. The initial partial pressure of the ethylene varied from about four-tenths of an atmosphere (Expts. 1, 3, 4) to about thirty centimeters of water (Expts. 5, 6), and varied greatly in single experiments, except in Expt. 6. This lack of constancy was due to decreasing vapor pressure of the solution, permitting more ethylene to enter, offset by the accumulation of any inert gas in the ethylene supply, and the production of hydrogen chloride. The difference in Expts. 3 and 4 could then be due to the difference in the volume of the gas phase in which the larger volume favored maintenance of a high ethylene partial pressure.

An attempt to hold this variable within narrow limits was made in subsequent experiments, by first filling the vapor phase with nitrogen to a total pressure of one atmosphere, and then allowing the ethylene to flow in at a pressure greater than this by 30 cm. of water. However, the rapidly decreasing chlorine partial pressure permitted the increase of the ethylene partial pressure, so that in Expt. 6 this was, in part, corrected for by closing the ethylene entrance periodically and opening the nitrogen entrance, thus allowing nitrogen to replace the accumulated ethylene in the gas phase. This was done six times during the experiment, and resulted in a marked increase in the proportion of chlorine reacting with the benzene. Any valid estimate of the ethylene partial pressure is impossible, but since the rate of solution of ethylene in benzene is low, and the rate of reaction is low, it may be assumed to be 30 ± 15 cm. of water in Expt. 6.

In diffused daylight (Expt. 2a) benzene alone reacts with chlorine at an appreciable rate (when shaken), but not in a darkened room (Expt. 2b). Experiment 1, then, cannot be compared strictly with subsequent experiments in which the reaction vessel as well as the room was darkened. The partial pressure of the ethylene appears to be an important factor in determining the proportion of chlorine reacting with benzene. Over 90% of the reacting chlorine reacts with benzene at low ethylene partial pressures. The effect of changing chlorine concentration upon this result has not yet been ascertained, but from the results given in Table I it would appear that at chlorine concentrations above 0.3 M the ethylene partial pressure is the major variable. No induction period was looked for. From previous work, the presence of oxygen would tend to reduce the length of any benzene–chlorine chain for a photochemically induced reaction, but its effect upon the ethylene-induced reaction is as yet undetermined. The walls have some effect upon the reaction, as evidenced by the low induction ratio in the homogeneous reactions as compared to the heterogeneous, and by the faster photochemical reaction in diffused light brought about by shaking.[7] However, immersed glass beads or glass wool

TABLE II

EXPERIMENTS WITH CHLORINE–BENZENE SOLUTIONS IN A SHAKER

Temp., 19–20'; concentration in moles per liter, volume of container, 116 cc. Conditions Expts. 1, 2a in diffused daylight, others in the dark. In Expts. 1, 3 and 4 ethylene was alone in the gas phase; Expts. 2a and 2b, air present; Expt. 5, 36 cc. of N_2 present; Expt. 6, 31 cc. of N_2 present at start, 43.7 cc. at end. Time in minutes, Expts. 1, 120; 2a, 450; 2b, 210; 3, 240; 4, 24; 5, 180: 6, —.

Expt.	Concn. of chlorine Initial	Final	Volumes (cc.) Solution,	g.	Moles of reactants Cl_2	C_2H_4	Ratio Cl_2/C_2H_4	Product, g.	Moles HCl at end
1	1.075	0.000	90	26	0.0968	0.0137	7.0	9.03	0.0138
2a	0.914	.187	88	28	,064	None	..	7.17	.0113
2b	1.242	1.228	..	..	...	None	..		...
3	1.250	0.337	104	12	.0950	.0145	6.65	7.3	.0161
4	1.42	.000	51	65	.0725	.0258	2.81	6.64	.0058
5	1.295	.151	48	68	.0550	.0077	7.14	3.01[a]	.0201[a]
6	1.295	.347	44	72	.0417	.00356	11.7	4.88	.0058

[a] In Expt. 5 the reaction mixture as a whole, instead of an aliquot portion, was treated with standard bisulfite and the excess bisulfite titrated with standard iodine as usual. The mixture then stood overnight before titrating the acid present. By morning this unusually large proportion of acid was present, and the yield of solid products, although cleanly crystalline, was lower than usual. It is thought that this may possibly be a function of the time of standing of the reaction mixture with water. Since the isolated products do not yield acid in contact with water, the experiment suggests either an unknown variable in the original reaction or possibly an unstable product first formed which reacts slowly with water to yield acid and water-soluble or volatile products, but which might change to water-stable products on standing. The isolated product did not appear to differ from that derived from other experiments, except that it was crystalline, whereas the presence of much acid is usually accompanied by gummy residues upon evaporation.

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[7] The effect of boiling the solution, mentioned by Luther and Goldberg (Ref. 3) may be related to an agitation factor.

have little or no effect, hence the gas–wall interface, if any, would appear to be the important one.

Preparation of Materials.—The ethylene was generated from ethylene dibromide and zinc, washed with alcohol and stored over water. A drying train including phosphorus pentoxide was interposed between the reservoir and the reaction flask. When necessary for accuracy in measuring the gas volumes, a nitrometer was used as a reservoir. Analysis showed up to 1% of air or other inert gas.

A tank of chlorine containing less than one mole per cent. of hydrogen chloride was used. Blackened bottles contained the benzene, into which the chlorine was passed slowly, usually overnight.

The benzene was distilled from chromic acid and sulfuric acid mixture, washed and distilled from solid potassium hydroxide and finally from sodium wire.

Analysis.—Benzene was saturated with ethylene in a bubbler and the ethylene pressure used to force the solution up into a pipet. The measured solution was then delivered below a bromine solution in carbon tetrachloride at −20°. After standing tightly stoppered in the dark for six hours (in two hours the reaction was 75% complete) the excess bromine was titrated, using aqueous potassium iodide and thiosulfate. Appropriate blanks showed no conflicting reactions with the benzene. At 22" the saturated solution was 0.084 *M*, and this value agreed closely with a direct measurement of the volume of gas dissolved. In the homogeneous reaction experiments the containers had a small gas phase to minimize volatilization. More dilute solutions were prepared by diluting the saturated stock solutions.

Chlorine in benzene cannot be analyzed for by adding aqueous potassium iodide and titrating the iodine. Errors as high as 30% are involved. The analysis was made by delivering pipetted samples below the surface of a known volume of standard 0.1 *N* sodium acid sulfite solution (standardized against iodine solution) and back-titrating the excess. The hydrogen chloride formed was estimated from the same sample by subsequently titrating the total acid present with standard alkali, using phenolphthalein, and subtracting from this total the acid found in the reaction

$$HSO_3^- + Cl_2(\text{or } I_2) + H_2O \longrightarrow SO_4^= + 2Cl^- (\text{or } I^-) + 3H^+$$

By suitable blanks the ratio (in equivalents) of acid formed to bisulfite used up was determined. It was usually very close to the theoretical value of 1.5, and constant. However, any error in this ratio caused a very large error in the acid calculated as formed in the reaction studied, and this, together with slight (1%) uncertainties in the analysis for chlorine, made the estimate of the amount of substitution very uncertain. The values given in the text are probably high.

The normality of a bisulfite solution is reasonably constant if the volume of solution is large, if air admitted to the solution is drawn through a similar solution, and if the buret and reservoir do not form a closed system. This last proviso eliminated some anomalous changes in normality, that is, each time the buret was emptied air from the room (not from the reservoir) was admitted to the buret. The difficulty seemed real and is probably connected with the auto-oxidation problem of sulfites.

The benzene hexachloride was purified and analyzed for chlorine; no evidence of the presence of $C_6H_5Cl_7$, which has similar properties and could have been formed, was observed.

Summary

Benzene hexachloride, together with substitution products, is formed when ethylene gas is passed into a benzene solution of chlorine in the dark. A mixture of the various stereoisomers is obtained, with the a-form (m. p.

157°) predominating. The molal ratio of total chlorine reacting to ethylene reacting varies from two to eleven in the present experiments, and is greater the lower the partial pressure of ethylene. This is explained on the basis of chain mechanisms for both the ethylene–chlorine and benzene–chlorine reactions, the latter being induced by and acting as an inhibitor of the former.

In homogeneous solution the above ratio, with chlorine in large excess, is approximately two. A higher proportion of the chlorine is used in substitution than in the heterogeneous reactions.

No evidence of a Friedel–Crafts type of reaction between the ethylene chloride formed and benzene could be found. In a mixture of benzene, benzoyl chloride and chlorine no benzophenone was formed with introduction of ethylene.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OR BRYN MAWR COLLEGE]

THE REDUCTION POTENTIALS OF SOME HIGHER BENZOLOGUES OF THE QUINONES

BY LOUIS F. FIESER AND EMMA M. DIETZ

RECEIVED JANUARY 15, 1931 PUBLISHED MARCH 6, 1931

With the view of applying certain new tests to the theories of the structure of anthracene, we have prepared three angular dibenz-anthraquinones,[1] and determined their reduction potentials. It seemed appropriate to include in this study other quinones derived from tetra- or pentacyclic hydrocarbons, and we have thus examined potentiometrically most of the known compounds of this type.

We were fortunate in securing a sample of picenequinone through the kindness of Professor Frederick D. Chattaway of Oxford University, while the chrysene used in the preparation of the 5,6-quinone was furnished by the Gesellschaft fur Teerverwertung through the courtesy of the late Dr. R. Weissgerber. The other derivatives of 5,6-chrysenequinone, as well as the 6,12-isomer, were prepared by the synthesis of Beschke and Diehm.[2]

The results of the electrometric titrations are summarized in the accompanying table. The nature of the titrating reagent indicates the method of titration employed; in most cases it was found expedient to reduce the quinone catalytically and to titrate the reductant with an oxidizing agent. While satisfactory results were easily obtained with the tetracyclic quinones, the very sparing solubility of the pentacyclic compounds presented a serious obstacle. With the very dilute solutions slight sources of error have a magnified effect upon the potentials. It

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[1] Fieser and Dietz, *Ber.*, *62*, 1827 (1929).

[2] Beschke and Diehm, *Ann.*, 384, 143 (1911).

TABLE I

REDUCTION POTENTIALS AT 25°

Solvent: 95% alcohol, *0 2 N* in HCl **and** *0 2 N* **in** LiCl

Quinone	Molality of quinone	Titrating agent[a]	**Normal potential E_0, v.**				ΔE_1, mv.	ΔE_2, mv.	E_0(av.), v.
1,2-Benzanthra-	0.0003	A	0.228	0.228	0.229		18.7	20.9	0.228
1,2,7,8-Dibenzanthra-	00006	B	.266	.264	.262		18 3	17.3	.264
1,2,5,6-Dibenzanthra-	.00013	A	.270	.265	.268		19 0	26 3	.268
(1,2)-Bz-3-metho-1,2,5,6-dibenzanthra-	.00015	A	.258	.259	.255		17 8	20.2	.257
5,6-Chrysene-	.0004	A,B	.465	.464	.466	0 464	18 9	19.1	.465
6,12-Chrysene-	.0001	B	,391	.393	.392	.393	17.9	17.9	.392
12-Hydroxy-5,6-chrysene-	.0001	B	.392	.391	.391		17.3	18.2	.391
12-Ethoxy-5,6-chrysene-	,0001	B	.418	.418	.419	.418	19.5	21 1	.418
1,2-Benz-3,4-anthra-[3]	.0001	C	,433	.428	.430	,430	18.6	20.2	.430
Picene-	,00006	B	.463	,477	.486	.470	57.0	71.0	.474±0.01

[a] Titrating agents: **A,** *p*-benzoquinone; B, tetrabromo-o-benzoquinone; C, 0.3 cc. of titanous chloride (20% solution) diluted to 50 cc. with the solvent.

was further found that electrode equilibrium was established very slowly in the titrations with these compounds; 'a steady value sometimes was reached only after a period of one hour. The consequent errors are reflected in the divergence of the separate determinations of the normal potential, E_0, particularly in the case of picenequinone. Because of the added uncertainty indicated by the wide deviation of the slope of the titration curve (ΔE_1 and ΔE_2) from the theoretical value ($\Delta E = 17.8$ mv.), the potential found for this compound is regarded as only an approximation.

The Structure **of Anthracene.**—It has been pointed out[4] that the abnormally low reduction potential of anthraquinone may be interpreted as an indication of the unusual reactivity of the anthracene nucleus. According to current theories, the seat of this reactivity may be either an ortho-quinonoid grouping of the double bonds or a para bond between the meso carbon atoms. While it is not easy to predicate the implications of the para-bond theory, for such a structure is purely hypothetical, the ortho-quinones are well-known substances and rational predictions of the properties of the benzologues of anthracene can be constructed from the assumption of the ortho-quinonoid structure of the hydrocarbon.

On the basis of this theory the attachment to anthrahydroquinone of a phenylene group in the angular position, as in I, should stabilize the

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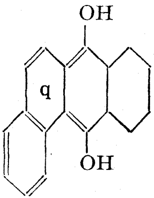
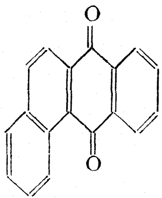
[3] Fieser and **Dietz,** THIS JOURNAL, 51, 3141 (1929).

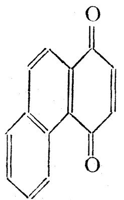
[4] Fieser and Ames, *ibid.*, 49, 2611 (1927).



I



II

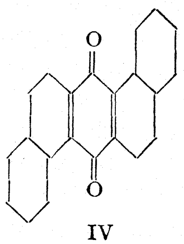


III

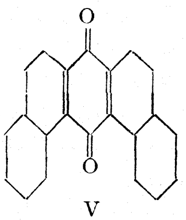
compound, in the sense of decreasing its tendency to undergo oxidation and thus relieve the tension in the ortho-quinonoid nucleus (q). This follows from the fact that β-naphthoquinone is more stable, in the same sense, than o-benzoquinone. This stabilizing effect of the added phenylene group would be expected to result in an increase in the oxidation–reduction potential of the system of which 1,2-benz-anthrahydroquinone is the reductant. The question of the possible influence of the extra benzene ring present in the oxidant, II, on the nature of the anthraquinone molecule can be readily answered by comparing 1,4-phenanthrenequinone, III, and 1,4-naphthoquinone. The latter compounds differ in just the way that 1,2-benz-anthraquinone differs from anthraquinone; a quinonoid ethylene linkage is in one case a part of a naphthalene ring, in the other case it is incorporated in a benzene nucleus. The potential of the naphthalene-containing compound, III, is the higher by 40 mv.[5]

If the extra phenylene group had no influence on the character of the reductant in question, the potential of the system from 1,2-benzanthraquinone would be expected to be 40 mv. higher than that from anthraquinone (E_0 = 0.155 v.),[6] or 0.195 v. The actual potential is 0.228 v., 73 mv. above that of the parent compound It is reasonable to attribute the extra increment to the stabilizing of the o-quinonoid system of the reductant, in the manner indicated.

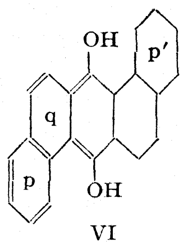
In the case of the dibenz-anthraquinones, IV and V, the second angular phenylene may be expected to have the same influence on the nature of the oxidant as the first such group, and this would give an increase in the potential of 40 mv. over that of 1,2-benzanthraquinone. Examination



IV



V



VI

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[5] Fieser, **This Journal**, 51, 3101 (1929). The difference in the potentials is erroneously reported in Table II of this paper as amounting to 30 mv.

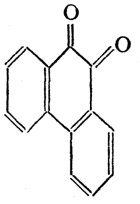
[6] Conant and Fieser, *ibid.*, 46, 1858 (1924).

of the o-quinonoid formula for one of the reductants, such as VI, reveals the fact that while the first phenylene group, p, is in a position to stabilize the quinonoid structure in the anthracene nucleus, the second group, p′, cannot be attached at the same time to the quinonoid ring and therefore cannot influence its reactivity. According to the theory, then, the angular dibenz-anthraquinones should differ in potential from the monobenz-derivatives by approximately 40 mv., and not by the larger figure of 73 **mv.** which represents the effect of a single phenylene group. The results given in the table show that the difference for the two quinones, IV and V, amounts to **36** mv. and 40 mv., respectively, and the good agreement with the predictions based upon the o-quinonoid theory of the structure of anthracene constitutes an argument in support of this theory.

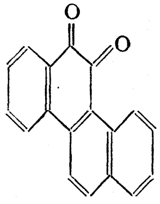
While the p-bond theory leads to no precise predictions of the effect of attaching an angular phenylene group to anthracene, it does imply that a second such group would have exactly the same influence as the first, for the p-bond formula is symmetrical. The present results show, however, that this is not the case and that, contrary to the *p*-bond theory, anthracene appears to have an unsymmetrical structure. It is unfortunate that the potential differences upon which these arguments are based are not more pronounced. The above conclusions appear justified, but they lack the weight to which they might otherwise lay claim.

The linear benz- and dibenz-anthraquinones offer an interesting field for a continuation of the present study, but it was found that these compounds, for reasons which will be apparent from a forthcoming publication, are not amenable to potentiometric study.

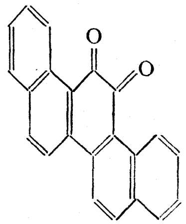
Benzologues of 9,10-Phenanthrenequinone.—5,6-Chrysenequinone, VIII, and picenequinone, IX, do not differ appreciably in potential from phenanthrenequinone, VII. While it is surprising that the added phenylene groups appear to have no influence, an adequate interpretation of the relationship will only be possible when the potential of the parent compound is more fully understood.



E_0 = 0.471 v.
VII



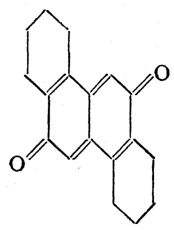
E_0 = 0.465 v.
VIII



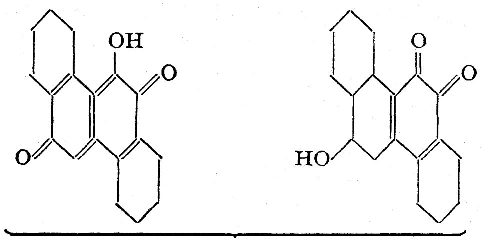
E_0 = 0 474 v.
IX

Amphi-chrysenequinone.—It is of interest to compare this substance, X, with amphi-naphthoquinone. The reduction potential of the latter compound has been estimated by an indirect method to be 0.758 mv.[7] By the inclusion of two of the quinonoid linkages of this substance in benzene rings the molecule is greatly stabilized and the potential is decreased by 0.366 v., or 0.183 v. for each such ring. This appears to be fairly consistent with the fact that the potential of *p*-benzoquinone is lowered 0.224 v. by the attachment to it of one phenylene group.

Hydroxy-chrysenequinone may conceivably exist in two tautomeric forms, XIa and XIb. Beschke and Diehm[2] have advanced chemical evidence in support of the ortho-quinonoid structure, XIb, and the electrochemical evidence confirms this view. If the structure of the compound were that of an amphi-quinone, the potential should be in the neighborhood of 0.120 v. below that of amphi-chrysenequinone (effect of a quinonoid hydroxyl), that is, about 0.272 v. Since this differs from the actual value by over 0.1 v. it is obvious that the amphi-quinonoid structure is excluded. If, on the other hand, the compound has the structure of XIb, it would be expected to differ in potential from ortho-chrysenequinone to about the same extent that 3-hydroxy-phenanthrenequinone differs from the unsubstituted quinone, or 0.053 v. The potential predicted on this basis is 0.465 − 0.053 = 0.412 v., and the figure is in fairly good agreement with the actual value of 0.391 v. The ortho-quinonoid formula is further supported by the fact that the ether, which is assuredly ortho-quinonoid, is just 0.027 v. higher in potential than the hydroxy compound. Such a relationship is entirely normal.



$E_0 = 0.392$ v.
X



$E_0 = 0.391$ v.
XIa XIb

While the structure of hydroxy-amphi-chrysenequinone is thus established beyond question, the potential of this substance presents a striking anomaly. When Beschke and Diehm prepared the compound for the first time, they advanced the view that the substance must exist in that tautomeric form which has the lower reduction potential. This general principle has been elaborated and applied in a number of instances by one of us,[8] and the generalizationinvariably has been confirmed. Beschke and Diehm had no means of estimating adequately the relative potentials

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[7] Fieser, THIS JOURNAL, 52, 5204 (1930).

[8] Fieser, *ibid.*, 50, 439 (1928).

of the two tautomeric forms, but it is now clear that they were in error in considering that the ortho-quinonoid form would have the lower potential. The present results show that the stable tautomer is the one having the higher reduction potential, and the case thus constitutes a definite exception to-the rule. The only suggestion which we can now offer in explanation of the failure of the hydroxyquinone to change over into a thermodynamically more stable tautomer is that there is some steric resistance to such a change.

Summary

A potentiometric study of the benzologues of anthraquinone and phenanthrenequinone has led to the following significant conclusions. (1) The potentials of the benz- and dibenz-anthraquinones lend support to the ortho-quinonoid theory of the structure of anthracene. (2) Hydroxy-chrysenequinone constitutes an exception to the rule that when a quinone can exist in two forms the one of lower potential will predominate.

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

THE OXIMES OF ALPHA, BETA-UNSATURATED KETONES AND THE BECKMANN REARRANGEMENT

BY A. H. BLATT

RECEIVED JANUARY 17, 1931 PUBLISHED MARCH 6, 1931

The work of Meisenheimer and others has brought into question the long-accepted assumption that in the Beckmann rearrangement a shift occurs between the oximino hydroxyl group and the hydrocarbon residue spatially adjacent—a cis migration—and has given new prominence to the view that the shift is between groups spatially removed—a *trans* migration. The original evidence to this effect was furnished by the ring opening of triphenyl isoxazole;[1] the bulk of the evidence, however, has come from the study of ring closure in appropriately substituted ketoximes.[2]

Although the chief evidence for the idea of a *trans* migration has come from the study of ring closure, there is one class of ketoximes, the oximes of α,β-unsaturated ketones, whose behavior seems incompatible with a *trans* migration.[3]

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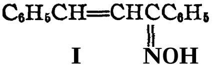
[1] Meisenheimer, *Ber.*, 54, 3206 (1921).

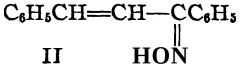
[2] Meisenheimer and Meis, *ibid.*, 57, 289 (1924); v. Auwers and Jordan, ibid., 57, 800 (1924); Brady and Bishop, J. *Chem.* Soc., 127, 1357 (1925); Meisenheimer, Zimmermann and Kummer, *Ann.*, 446, 208 (1926).

[3] Von Auwers has discussed these oximes in a preliminary notice [*Ber.*, 62, 1320 (1929)] and has outlined a series of researches on the oxime configurations and the relation between configuration, substituents and ease of ring closure. The present work was outlined and started several years ago It was completed recently without knowl-

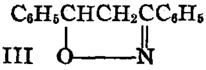
Two α,β-unsaturated ketones, benzalacetophenone[4] and dypnone[6] have been studied in some detail. Since the facts are similar in both cases it will be necessary to review only the former. When benzalacetophenone is treated with hydroxylamine hydrochloride, the product is an oxime. To this oxime, which furnishes cinnamanilide when it undergoes the Beckmann rearrangement, Henrich, on the basis of a cis migration, assigned the structure (I) and the designation of labile oxime.


$C_6H_5CH{=}CH\underset{NOH}{\underset{\|}{C}}C_6H_5$

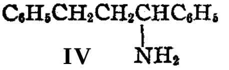
I


$C_6H_5CH{=}CH{-}\underset{HON}{\underset{\|}{C}}C_6H_5$

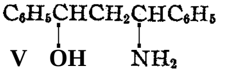
II


$C_6H_5\underset{O\text{———}}{\underset{|}{CH}}CH_2\underset{N}{\underset{\|}{C}}C_6H_5$

III


$C_6H_5CH_2CH_2\underset{NH_2}{\underset{|}{CH}}C_6H_5$

IV


$C_6H_5\underset{OH}{\underset{|}{CH}}CH_2\underset{NH_2}{\underset{|}{CH}}C_6H_5$

V

When benzalacetophenone is treated with hydroxylamine hydrochloride and an excess of alkali it furnishes, in poor yield and among other products, a substance which Henrich formulated as the isomeric stable oxime (II). This stable oxime, however, is surprisingly unreactive. In contrast to the labile oxime it does not yield an acetyl derivative, nor does it give an addition product with phenyl isocyanate, nor can it be made to undergo a Beckmann rearrangement. In view of its unreactivity Henrich considered an alternative formulation as 3,5-diphenyl isoxazoline (III). This cyclic formula, however, he rejected because he felt it to be inconsistent with the fact that on reduction with sodium and boiling alcohol both the stable and labile oximes give the same product (IV), whereas in Henrich's opinion the isoxazoline should have given the amino alcohol (V). This behavior on reduction has not seemed to the present writer to be sufficient for the rejection of the isoxazoline formula, inasmuch as so little is known of the general behavior on reduction of this type of heterocyclic compounds. And since a decision between the oxime and isoxazoline formulas is a prerequisite for further discussion, our experiments started with this question.

Most of the workers who preceded Henrich had used the isoxazoline formula for the stable oxime and Claus[4c] had shown that this stable oxime could be oxidized to the known 3,5-diphenyl isoxazole—a fact which at least balances Henrich's reduction as structural evidence. To decide definitely between the oxime and isoxazoline formulas we treated the stable oxime with methylmagnesium iodide after the method of Zerewitinoff, believing that no matter how inert the oximino hydroxyl group it

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edge of v. Auwers' notice. When the writer's attention was called to the bibliographical omission he informed Professor v. Auwers of this work.

[4] (a) Rupe and Schneider, *Ber.*, 28, 965 (1895); (b) Goldschmidt, *ibid.*, 28, 986 (1895); (c) Claus, *J. prakt. Chem.*, [2] 54, 408 (1896); (d) Fleck, "Dissertation." Leipzig, 1903; the work dealing especially with the rearrangement is by Henrich, (e) *Ann.*, 351, 171 (1907); (f) *Ber.*, 44, 1533 (1911).

[5] (a) Henrich and Wirth, *ibid.*, 37, 732 (1904); (b) *Monatsh.*, 25, 423 (1904). See also references 4e and 4f.

should certainly evolve methane with this reagent. However, the stable oxime from benzalacetophenone yields no gas; hence it has no active hydrogen and it is to be written, therefore, as the isoxazoline (III).

The facts now available are that benzalacetophenone in acid solution yields an oxime, in alkaline solution an isoxazoline. The inferences from these facts are that the true oxime has the syn phenyl configuration (I) assigned it by Henrich, that the isomeric oxime is unstable and on formation goes into the isoxazoline (111), and that in the Beckmann rearrangement of the true oxime there is a cis shift between the hydroxyl and phenyl groups. A more detailed study for the purpose either of confirming these inferences or of discovering new facts which would bring the rearrangement of α,β-unsaturated ketoximes into line with the other oximes constitutes the balance of this article.

I. The Configuration of the True Oximes

For determining whether the true oximes of α,β-unsaturated ketones possess the *syn* phenyl configuration, corresponding to (I), or the ***anti*** phenyl configuration, corresponding to (II), benzalacetophenone oxime is unsatisfactory; it is obtained in poor yield, it crystallizes with difficulty, and the cyclic products to be expected from it are symmetrical and give no clue to the way in which ring closure has taken place. Consequently we turned to other unsaturated ketones, benzal-*p*-bromo-acetophenone and benzal-o-chloro-acetophenone, and prepared from them the corresponding true oximes—that is, oximes which on rearrangement give substituted anilides of cinnamic acid.

The oxime of benzal-o-chloro-acetophenone, if it has the *syn* phenyl structure (VI), corresponding to that assigned by Henrich to the true oxime of benzalacetophenone, might be expected to lose halogen acid when treated with alkali and yield a benzisoxazole. Actually it does not lose halogen acid even on prolonged boiling with alcoholic potash. This fact, while not conclusive, because of the possible inactivity of the chlorine, does make necessary serious consideration of the alternative configuration. Using the more readily available oxime of benzal-*p*-bromo-acetophenone it was possible to secure definite evidence as to configuration by closing the ring on the side toward the double bond. When this oxime is brominated in chloroform solution it takes up two atoms of bromine, yielding a dibromide (VIII), which either by the action of alkali or of heat loses hydrogen bromide and is converted into 3-#-bromophenyl-5-phenyl isoxazole (IX). The structure of the isoxazole was shown by its synthesis from the dibromide of benzal-*p*-bromo-acetophenone.[6] This ring closure is explicable only if the oxime has the ***anti*** phenyl configuration (VII).

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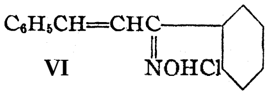
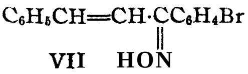
[6] **Weygand and Bauer**, *Ann.*, 457, 123 (1927).

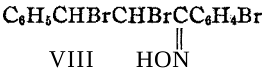


VI



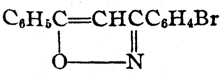
$C_6H_5CH{=}CH{\cdot}\underset{\underset{\text{HON}}{\|}}{C}C_6H_4Br$

VII



$C_6H_5CHBrCHBr\underset{\underset{\text{HON}}{\|}}{C}C_6H_4Br$

VIII



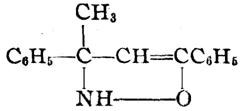
IX

Since the oxime (VII) is the analog of all the oximes of α,β-unsaturated ketones so far examined (it like all the others gives an anilide of cinnamic acid on rearrangement), one must conclude that the true oximes of these α,β-unsaturated ketones have the *anti* phenyl configuration and undergo a *trans* shift in the Beckmann rearrangement.

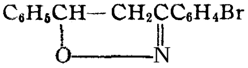
II. The Mechanism of Formation of the Isoxazolines

With the *anti* phenyl configuration assigned to the true α,β-unsaturated ketoximes, it becomes of interest to learn whether these oximes are intermediate steps in the formation of the isoxazolines. We have, therefore, treated the true oximes of dypnone and of benzal-p-bromoacetophenone with hydroxylamine hydrochloride and excess alkali (the conditions under which the isoxazolines are formed directly from the ketones) and found that the oximes are unaffected. Neither are they converted into isoxazolines by heating with alcoholic alkali. It would seem then that the oximes are not intermediate in the formation of the isoxazolines.

Since the isoxazolines are formed directly from the ketones only in alkaline solution and since free hydroxylamine is known to add to unsaturated carbonyl compounds,[7] the 1,4-addition of the reagent followed by ring closure immediately suggests itself as a possible mechanism. This mechanism can be tested in the case of dypnone for here the isoxazoline if formed through simple 1,4-addition would have the structure (X), and it would possess an active hydrogen atom. Actually the isoxazoline is inert toward the Grignard reagent.



X



XI

Similarly, if the isoxazoline from benzal-*p*-bromo-acetophenone were formed through 1,4-addition, the nitrogen would be attached to the carbon atom adjacent to the phenyl group. Actually, the nitrogen is attached to the carbon atom adjacent to the *p*-bromophenyl group (XI), as is shown by the oxidation of the isoxazoline to 3-*p*-bromophenyl-5-phenyl isoxazole (IX). Consequently, the simple 1,4-addition of hydroxylamine is eliminated as a mechanism.

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[7] Posner, *Ann.*, 389, 1 (1912).

It appears likely that the isoxazolines are formed as a result of a rather complex process, perhaps involving the addition of a molecule of hydroxylamine to two molecules of unsaturated ketone.[4d] For the present, however, it must suffice to emphasize, in view of the *anti* phenyl configuration assigned to the true oximes, that these oximes are not intermediates in the formation of the isoxazolines.

III. The Sulfuric Acid Rearrangement of the Oximes

Since it has been established that the so-called stable oximes of α,β-unsaturated ketones are in reality isoxazolines, a reaction first noted by Henrich[4e] must be reinterpreted. Henrich showed that the true oximes of benzalacetophenone and dypnone when dissolved in concd. sulfuric acid, heated and then poured on ice gave the stable oximes; restated, the true oximes rearrange to isoxazolines. This is, in effect, a new type of oxime rearrangement. We have confirmed Henrich's observations using dypnone and have further found that in this and other cases simple solution in sulfuric acid followed by pouring on ice suffices to bring about the rearrangement. The reaction is a remarkably clean one. In fact, since the oximes are the sole reaction product using the ketone and hydroxylamine hydrochloride, while the isoxazolines are only one of the many products formed in alkaline solution, it is frequently more satisfactory to prepare the isoxazolines via the oximes and sulfuric acid than from the ketones directly.

It is, of course, hazardous to use this rearrangement as structural evidence but it may be pointed out that the rearrangement is certainly not incompatible with the anti phenyl configuration. From appearances at least the rearrangement would seem to involve halochromic salt formation on the part of the oxime, followed by rearrangement of the cation in the strongly acid medium to yield a more basic product.

The expenses of this research have been defrayed by funds privately contributed.

Experimental Part

$C_6H_5CH{=}CHCOC_6H_5$ and $C_6H_5C(CH_3){=}CHCOC_6H_5$

3,5-Diphenyl isoxazoline and **3,5-diphenyl-5-methyl** isoxazoline were prepared according to the directions of previous workers.[4c,e] Treated in a Zerewitinoff apparatus with an excess (6 moles) of methylmagnesium iodide in isoamyl ether, there was no evolution of gas even on warming.

When dypnone oxime, prepared according to Henrich's directions,[4e] was boiled with alcoholic sodium hydroxide—2.0 g. of oxime in 150 cc. of alcohol containing 1.5 g. of sodium hydroxide—80% of the oxime was recovered. No isoxazoline could be detected.

Another sample of dypnone oxime was shaken with a small volume of concd. sulfuric acid. There was a noticeable evolution of heat as the oxime dissolved to yield a deep yellow solution. As soon as all the material had gone into solution the reaction mixture was poured onto cracked ice. The precipitated solid melted, after drying, at 75–78°

and a mixture with the pure 3,5-diphenyl-5-methyl isoxazoline (78°) melted at 77–78°. The yield was quantitative.

$C_6H_5CH{=}CHCOC_6H_4Cl$-*o*[8]

The unsaturated ketone was made by condensing benzaldehyde and o-chloro-acetophenone according to the directions in "Organic Syntheses" for benzalacetophenone.[9] The *o*-chloro-acetophenone was obtained by the hydrolysis of ethyl o-chlorobenzoyl acetate.[10] Since the benzal-*o*-chloro-acetophenone, which was obtained in good yield as a yellow oil, could not be induced to crystallize, it was converted directly to the oxime. For this purpose 12.12 g. of unsaturated ketone was dissolved in 100 cc. of alcohol and 7.0 g. of hydroxylamine hydrochloride (100% excess) in 25 cc. of water was added. The resulting solution was boiled for five hours, left overnight, then ether and water were added. The ether layer was worked up in the usual manner and yielded the oxime upon slow evaporation after the addition of petroleum ether. The oxime is reluctant to crystallize and the yield is poor. For analysis the material was twice crystallized from ether and petroleum ether.

Anal. Calcd. for $C_{15}H_{12}ONCl$: C, 69.9; H, 4.7. Found: C, 69.8; H, 4.8.

Benzal-*o*-chloro-acetophenone oxime crystallizes in small cubes. It is very soluble in all the common solvents save petroleum ether. On melting, this oxime shows a peculiar behavior; the most carefully purified material melts over a wide range, 110–124° heating at a rate of 2° per minute, to give a yellow melt; compare the behavior of the oxime of benzal-*p*-bromo-acetophenone below.

Beckmann Rearrangement.—Phosphorus pentachloride in excess was added to 1.0 g. of the oxime dissolved in 10 cc. of absolute ether. The reaction flask was cooled in ice water until the initial precipitate had redissolved, then the solution was poured on ice and the product taken up in ether. On evaporation of the ether, white crystals melting at 134–136° were obtained. These crystals did not depress the melting point of a sample of the o-chloro-anilide of cinnamic acid prepared from the acid chloride and *o*-chloro-aniline.

Anal. Calcd. for $C_{15}H_{12}ONCl$: C, 69.9; H, 4.7. Found: C, 69.8; H, 4.8.

The o-chloro-anilide of cinnamic acid is quite soluble in acetone and ether. It crystallizes well from methyl and ethyl alcohols in very fine colorless needles when its solutions in these solvents are diluted with hot water. The anilide melts at 136–137°.

Action of Alkali on the Oxime.—To a solution of 2.0 g. of potassium hydroxide in 25 cc. of methyl alcohol there was added 0.761 g. of oxime. The reaction mixture was boiled for five and one-half hours, during which time a red color developed. The solution was then diluted with 125 cc. of water, acidified with dilute nitric acid and left overnight. Next day the precipitate was removed by filtration and the chloride ion in the filtrate determined by a Volhard titration. Only 0.69 cc. of 0.1 N silver nitrate solution—corresponding to the removal of 2.3% of the chlorine—was required. The precipitate weighed 0.70 g. and when crystallized slowly from ether and petroleum ether it yielded the characteristic cubes of the original oxime, which was identified by a melting point and a mixed melting point determination.

$C_6H_5CH{=}CHCOC_6H_4Br$-*p*

Preparation of the Oxime.—A solution of 0.05 mole of unsaturated ketone was prepared by dissolving 14.35 g. of the ketone in 150 cc. of hot alcohol. After the addition of a drop of hydrochloric acid to neutralize any alkali occluded during the preparation of

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[8] The preliminary experiments with this ketone were done by Mr. M. Bovarnick.

[9] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1922, Vol. II, p. 1.

[10] Thorp and Brunskill, THIS JOURNAL, 37, 1258 (1915).

the ketone, 5.3 g. (0.075 mole) of hydroxylamine hydrochloride dissolved in 25 cc. of water was added and the reaction mixture boiled for four hours. Hot water was then added to incipient cloudiness. On cooling, the oxime crystallized in fine white needles. which were filtered and dried. The yield was 13.0 g. or 86%. By concentrating the filtrate and adding water another gram of material was obtained. For analysis the oxime was recrystallized from alcohol.

Anal. Calcd. for $C_{15}H_{12}ONBr$: C, 59.6; H, 4.0. Found: C, 59.7; H, 4.0.

Benzal-*p*-bromo-acetophenone oxime (VII) is quite soluble in the common organic solvents; crystallizes well from 95% alcohol or more dilute alcohol in extremely fine needles. These needles—perfectly colorless—melt over a wide range, 138–150°, to a yellow liquid. Repeated crystallization does not affect the melting point and a fractional crystallization accompanied by a microscopic examination of the crystals showed them to be homogeneous. A small sample of the pure oxime was kept at 150° for one-half hour. During this time an odor of benzaldehyde or benzonitrile was noticeable. The yellow melt, on cooling, gave a solid discolored yellow, apparently the oxime accompanied by decomposition products. No isoxazoline could be detected.

Action of Alcoholic Alkali on the Oxime.—Two grams of the oxime was dissolved in 25 cc. of alcohol containing 2.0 g. of potassium hydroxide and the solution was boiled for four hours. It developed a yellow color and an odor indicating that some hydrolysis had taken place. However, by adding water to complete precipitation, 1.75 g. of oxime was recovered and there was no evidence of the formation of isoxazoline.

Action of Hydroxylamine on the Oxime.—When 3.0 g. of the oxime was dissolved in 35 cc. of hot alcohol, a solution of 1.05 g. of hydroxylamine hydrochloride and 2.0 g. of potassium hydroxide in 10 cc. of water added, and the reaction mixture boiled for three hours there was no conversion to the isoxazoline. On working up the products of the reaction 80% of the oxime was recovered.

Beckmann Rearrangement.—Phosphorus pentachloride in excess was added to 2.0 g. of the oxime in 25 cc. of absolute ether. After the initial precipitate had redissolved the reaction mixture was poured onto ice, ether added and the ethereal solution washed with water, sodium carbonate solution and dried. On evaporation of the ether, 1.6 g. of solid, discolored yellow, was obtained. This material was purified by crystallization from alcohol. It then melted at 188–189°. The *p*-bromo-anilide of cinnamic acid was prepared from the acid chloride and *p*-bromo-aniline. It melted at 191° and a mixed melting point with the rearrangement product was 189–190°.

Anal. Calcd. for $C_{15}H_{12}ONBr$: C, 59.6; H, 4.0. Found: C, 59.3; H, 4.1.

Bromination of the Oxime.—When 5.2 g. of the oxime was dissolved in 100 cc. of chloroform and 2.8 g. of bromine in the same solvent was added, a dibromo-oxime (VIII) was formed. The crude material, obtained by pumping off the chloroform, weighed 7.3 g., was discolored red and melted with vigorous decomposition at about 150°. It was purified by crystallization from chloroform and petroleum ether, from which it separates in splendid clusters of fine needles melting, with decomposition, at about 155°.

Anal. Calcd. for $C_{15}H_{12}ONBr_3$: Br, 51.9. Found: Br, 51.3.

The dibromo-oxime is difficultly soluble in the ordinary solvents and if their boiling points are at all elevated it seems either to react with the solvent or to lose hydrogen bromide. With alcoholic alkali the dibromo-oxime eliminates hydrogen bromide to yield 3-p-bromophenyl-5-phenyl isoxazole (IX) but the reaction is not clean cut—doubtless because the greater part of the material follows the more complex course recently outlined for α,β-dibromo ketones by Kohler and Addinall.[11] Thus when

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[11] Kohler and Addinall, THIS JOURNAL, 52,3728 (1930).

0.842 g. of dibromo-oxime was added to 25 cc. of hot methyl alcohol containing 2.0 g. of potassium hydroxide, a brilliant orange solution resulted. Some of the material seemed not to enter into the reaction but to persist as a heavy oil; the oxime is only slightly soluble in methanel. Soon after the addition of the dibromide glistening flat plates of isoxazole began to separate from the solution. After three hours' boiling the reaction mixture was diluted to 150 cc. with distilled water and left overnight. Next day it was acidified with dilute nitric acid, which discharged the color, and filtered. The filtrate in a Volhard titration required 31.75 cc. of 0.1 N silver nitrate solution, corresponding to the elimination of 87% of the aliphatic bromine in the dibromide. The precipitate when crystallized from hot ethyl acetate yielded 0.1 g. of 3-*p*-bromophenyl-5-phenyl isoxazole (IX), which was identified by its melting point, 178–179°, and a mixed melting point with a specimen prepared from the dibromide of benzal-*p*-bromo-acetophenone—see below. The ethyl acetate filtrate contained material which gave a copper salt with aqueous copper acetate.

Action of Heat on the **Dibromo-oxime (VIII).**—Either as the pure solid or in solution the dibromo-oxime when heated loses hydrogen bromide to form the isoxazole (IX). One gram of pure dibromide in a small flask connected to a water pump was heated to 150° until the evolution of hydrogen bromide ceased. The evolved gases reddened litmus paper and produced a yellow precipitate when passed into silver nitrate solution. The dark red melt solidified on cooling. It was crystallized from acetic acid and yielded 0.3 g. of isoxazole. The filtrates deposited an additional small quantity of isoxazole. The isoxazole was identified by its melting point and a mixed melting point. The yield was 50%. The same conversion to the isoxazole can be brought about by heating the dibromo-oxime in glacial acetic acid. Thus 0.5 g. of the dibromooxime in 20 cc. of glacial acetic acid was boiled for thirty minutes. On concentrating and cooling the solution 0.17 g. of isoxazole was obtained.

Synthesis of **3-*p*-bromophenyl-5-phenyl-isoxazole (IX).**—To a suspension of 8.9 g. of the dibromide of benzal-*p*-bromo-acetophenone[12] and 2.8 g. of hydroxylamine hydrochloride in 150 cc. of alcohol, there was added 6.6 g. of potassium hydroxide in 15 cc. of water. A yellow color immediately developed and in a few minutes glistening white plates resembling naphthalene began to precipitate. After forty-five minutes the reaction mixture was cooled and filtered, then the precipitate washed thoroughly with water and dried. The yield of crude material, which was practically pure, was 3.6 g For analysis the isoxazole was crystallized from ethyl acetate.

Anal. Calcd. for $C_{16}H_{10}ONBr$: C, 60.0; H, 3.3. Found: C, 60.0; H, 3.7.

3-p-Bromophenyl-5-phenyl isoxazole (IX) is insoluble in cold alcohol and ether, slightly soluble in acetone and chloroform. It crystallizes well from glacial acetic acid, benzene or ethyl acetate. The pure material melts at 178–179°.

Preparation of 3-p-Bromophenyl-5-phenyl **Isoxazoline** (XI). A. From the Ketone.—A solution of 2.1 g. of hydroxylamine hydrochloride (0.03 mole) and 4.0 g. of potassium hydroxide in 20 cc. of water was added to a solution of 5.6 g. of benzal-p-bromo-acetophenone (0.02 mole) in 70 cc. of alcohol. After boiling for one and one-half hours, during which time the solution turned orange in color while colorless glistening crystals began separating, the reaction mixture was left overnight. Next day the precipitate of isoxazoline was filtered and dried; yield, 1.9 g. or 30%. The filtrate on dilution with water yielded other products which in view of the known complexity of the alkaline reaction were not studied.

B. From the **Oxime.**—One gram of benzal-*p*-bromo-acetophenone oxime was shaken with 20 cc. of concd. sulfuric acid. The oxime dissolved giving a yellow solution.

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[12] Weygand and Bauer, ***Ann.,*** 459, 138 (1927).

After standing overnight the sulfuric acid was poured onto ice and the colorless precipitate filtered and dried. It weighed 0.85 g., melted at 137–139° and caused no depression in the melting point of the isoxazoline prepared directly from the ketone. For analysis the material was crystallized from alcohol.

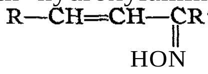
Anal. Calcd. for $C_{15}H_{12}ONBr$: C, 59.6; H, 4.0. Found: C, 59.7; H, 4.2.

3-*p*-Bromophenyl-5-phenyl-isoxazoline (XI) is moderately soluble in and crystallizes well from the ordinary solvents. In appearance the glistening flat plates of the isoxazoline closely resemble the isoxazole. However, the solubility of the isoxazoline in alcohol is considerably greater than the isoxazole. The pure isoxazoline melts at 138–139°.

Oxidation of the Isoxazoline (XI) to the Isoxazole (IX).—A solution of 2.0 g. of the isoxazoline in 100 cc. of glacial acetic acid was heated to 80° and 1.3 g. (200% excess) of chromic oxide was added. The reaction mixture was stirred for forty-five minutes, then poured into 400 cc. of cold water. The resulting precipitate was filtered and washed with water and a small amount of cold alcohol. It was then boiled with an amount of alcohol insufficient for complete solution. The hot alcoholic solution was separated from the solid residue by filtration. The residue crystallized from ethyl acetate furnished 0.25 g. of pure isoxazole. The first crop of crystals from the alcoholic filtrate was likewise isoxazole and weighed 0.25 g. The identity of these two sets of material was shown by a mixed melting point with the pure isoxazole. The second and third crops of crystals from the alcoholic filtrate weighed 0.6 g. and were slightly impure isoxazoline, as shown by their melting points. The balance of the material apparently had been further oxidized.

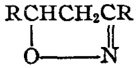
Summary

Certain α,β-unsaturated ketones when treated with hydroxylamine hydrochloride yield oximes of the general configuration



$$R{-}CH{=}CH{-}\underset{\underset{HON}{\|}}{C}R'$$

. These oximes undergo a *trans* shift in the Beckmann rearrangement and when dissolved in concd. sulfuric acid rearrange in a different manner to yield the isomeric isoxazolines



$$\begin{array}{l}RCHCH_2CR' \\ \;\;|\qquad\quad \| \\ \;\;O{-}{-}{-}{-}N\end{array}$$

. The so-called stable oximes of these α,β-unsaturated ketones are in reality isoxazolines, and are formed through a process which does not involve either the true oxime as an intermediate or the simple 1,4-addition of hydroxylamine to the ketone.

BUFFALO, NEW YORK

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

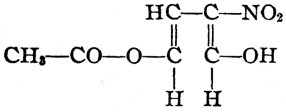
THE STRUCTURE OF NITROFURAN AND THE MECHANISM OF NITRATION IN THE FURAN SERIES

BY B. T. FREURE AND JOHN R. JOHNSON

RECEIVED JANUARY 19, 1931 PUBLISHED MARCH 6, 1931

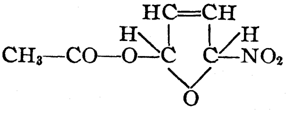
The nitration of furoic acid,[1] furfural diacetate,[2] 2-methylfuran[3] and many other furan derivatives, leads to the formation of nitro compounds in which it is reasonably certain that the nitro group has entered an *alpha* position. The nitration of furan itself gives a crystalline nitrofuran which Marquis[4] has formulated as β-nitrofuran. Since his work does not constitute an unequivocal demonstration of the position of the nitro group, and a large amount of indirect evidence would lead one to expect an α-nitrofuran, the validity of his formula is doubtful. The present study was undertaken with the object of establishing the structure of this nitrofuran and elucidating the mechanism of the nitration process.

In the nitration of furan, which is effected in the presence of acetic anhydride, there is formed an intermediate nitroacetate. This product corresponds in composition to the addition of a molecule of nitric acid and a molecule of acetic acid, with the elimination of a molecule of water. On treatment with pyridine, the unstable nitroacetate loses a molecule of acetic acid and is transformed into a crystalline nitrofuran. Marquis[4] found that the intermediate nitroacetate is decomposed by warm water with the production of nitrous and acetic acids and maleic dialdehyde, and this observation led him to formulate the intermediate product as an open-chain enol (I), produced by rupturing the oxygen bridge of the furan ring. It is difficult to concede that the formation of maleic dialdehyde is valid evidence for assigning the nitro group to the β-position and for assuming an open-chain enol structure. It seems more reasonable to assign to the intermediate nitroacetate a closed chain structure (II), which would be produced by 1,4-addition of nitric acid and subsequent acetylation. A similar 1,2-addition would give an alternative closed chain structure (III).

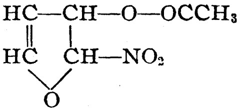


$$\begin{array}{ccc} & HC & C\text{—}NO_2 \\ & \| & \| \\ CH_3\text{—}CO\text{—}O\text{—} & C & C\text{—}OH \\ & | & | \\ & H & H \end{array}$$

I



II



III

The formation of maleic dialdehyde can be explained more simply from the ring structures (II and III) than from the open-chain enol (I)

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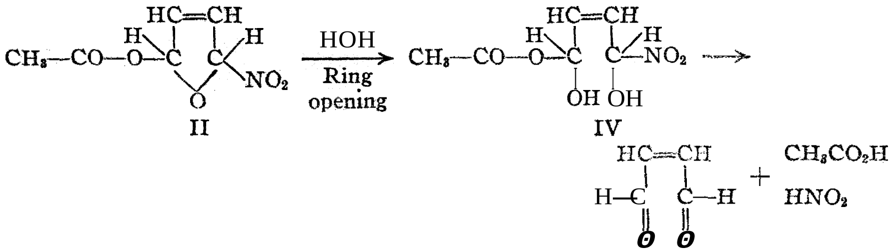
[1] Rinkes, *Rec. trav. chim.*, 49, 1167 (1930).

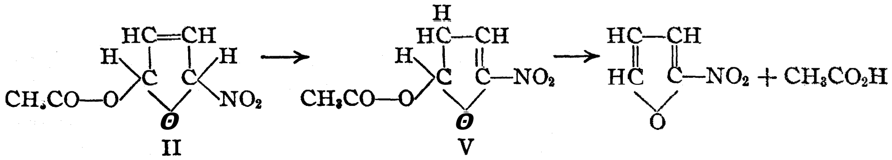
[2] Gilman and Wright, THIS JOURNAL, 52, 2550 (1930).

[3] Ref. 1, p. 1118.

[4] Marquis, *Ann. chim. phys.*, [8] 4, 216 (1905).

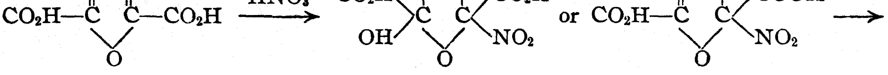


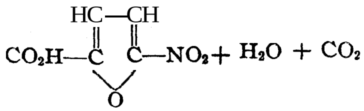
The decomposition of the unstable α-hydroxy nitro compound (IV) into an aldehyde and nitrous acid is analogous to the transformation of a-hydroxycarboxylic and α-hydroxysulfonic acids into aldehydes. The transformation of the intermediate nitroacetate (II) into 2-nitrofuran by the action of pyridine can be explained by 1,4-elimination of acetic acid or by a preliminary rearrangement into an isomeric nitroacetate (V), followed by 1,2-elimination of acetic acid



This type of rearrangement may be expected to occur readily since this shift of the double bond brings it into conjugation with the double bond of the nitro group. This reaction is analogous to the migration of the double bond from the β,γ- to the α,β-position in unsaturated carboxylic acids.

The behavior of certain substituted furan derivatives on nitration furnishes additional evidence for the formulation of the intermediate product as a ring compound. Although esters of furoic and furylacrylic acids form intermediate nitroacetates, the free acids do not form any intermediate product that can be isolated. It is highly probable that this difference is due to a greater lability of the intermediate product rather than to a fundamental difference in the mechanism of nitration. This view is supported by the observation that the nitration of furan derivatives containing a carboxyl group in the alpha-position often results in a displacement of the carboxyl group by the nitro group. Since the esters of these acids do not show this behavior, the decarboxylation is readily explained by the great instability of the intermediate a-nitro carboxylic acid





There is at present no direct evidence that favors the postulation of 1,4-addition of nitric acid rather than 1,2-addition. In the course of the present work one of the intermediate nitro compounds (obtained from methyl furoate) has been isolated in a pure state as a stable white crystalline solid. We hope to determine the structure of this intermediate compound in order to ascertain whether 1,4- or 1,2-addition has taken place.

In establishing the structure of the nitrofuran obtained by Marquis, 5-nitrofuroic acid was used as a reference substance. The position of the nitro group in this compound has been established with reasonable certainty by its formation from dehydromucic acid (furan-2,5-dicarboxylic acid) through the displacement of one carboxyl group and from 5-sulfofuroic acid through displacement of the sulfonic acid group.[5] It should suffice, therefore, to decarboxylate 5-nitrofuroic acid and to compare the resulting 2-nitrofuran with the compound produced by the direct nitration of furan. Accordingly, nitrofuroic acid (m. p. 185–185.5°) was decarboxylated by heating with copper bronze, in the presence of organic bases. The resulting 2-nitrofuran (m. p. 28.8–29.2°) proved to be identical with a specimen of nitrofuran (m. p, 28.8–29.2°) obtained from furan by nitration. Consequently, the nitrofuran described by Marquis should be designated as 2-nitrofuran instead of 3-nitrofuran.[6] Thus the nitration of furan occurs in an alpha position, in conformity with many furan derivatives and with its sulfur analog, thiophene.

Experimental

5-Nitrofuroic Acid.—This acid was prepared by hydrolysis of methyl or ethyl 5-nitrofuroate with strong sulfuric acid. Our experience showed that the yields were improved by using a solution of two parts by volume of concd. sulfuric acid in three parts of water, instead of the more concentrated acid (1:1) used by Marquis. In a typical preparation 55 g. of pure methyl 5-nitrofuroate was refluxed for fifty minutes with a solution of 250 cc. of concd. sulfuric acid in 375 cc. of water. The resulting 5-nitrofuroic acid after recrystallization from hot water melted at 185–185.5° (corr.) and weighed 40 g. (79% yield).

Intermediate Nitroacetate from Methyl Furoate.—In studying the nitration of

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[5] Hill and White, *Am. Chem. J.*, 27, **193** (1902).

[6] This result has been anticipated by Rinkes (Ref. 1) who obtained a nitrofuran. m. p. 27.9°, by displacement of the carboxyl group of 2-furoic acid. He concluded that this product was 2-nitrofuran and showed that it was identical with the nitrofuran obtained by nitration of furan. To the intermediate nitroacetate, Rinkes assigns an open-chain enol formula which differs from that of Marquis merely in the position of the nitro group. We prefer to assign to this intermediate product a structure which differs from that of Marquis in the position of the nitro group and in having a closed chain (dihydrofuran) structure.

methyl furoate in acetic anhydride, it was observed that a white crystalline intermediate product could be obtained, along with a liquid product, if the excess of acetic anhydride was removed by prolonged contact with water. Although Marquis has described methyl 5-nitrofuroate, he did not report the isolation of this crystalline intermediate product.

A cooled solution of 50 g. of pure methyl furoate in 75 g. of acetic anhydride was added to a solution of 125 g. of fuming nitric acid (sp. gr. 1.50) in *200* g. of acetic anhydride, prepared and maintained at −5°. The temperature of the reaction mixture was kept at −5° during the course of this addition (two hours) and the resulting solution was stirred at −5° for two hours after all of the methyl furoate had been added. The reaction mixture was poured onto 500 g. of cracked ice and **2.5–3** liters of water was added. After stirring vigorously for twenty to thirty minutes the original viscous oil changed to a waxy mass containing white crystals and adhering drops of oil. This mass was separated and washed thoroughly, by stirring with cold water until the washings were free from acid. The waxy mass was pressed thoroughly on a suction filter in order to free the crystals from the adhering oil. The crystalline portion was washed with cold sodium bicarbonate solution and freed from alkali by repeated washing with cold water. After purification by several crystallizations from absolute methyl alcohol, the intermediate nitroacetate formed colorless needles which melted at **95.9°** (corr.) in a capillary tube; on the electric bar[7] the crystals melted at 96.3° (corr.). This compound is very slightly soluble in petroleum benzine, and sparingly soluble in cold ether, carbon tetrachloride and methyl or ethyl alcohol. It is very soluble in acetone and in hot methyl or ethyl alcohol and glacial acetic acid.

Anal. Calcd. for $C_8H_9O_7N$: C, 41.54; **H, 3.93.** Found: C, 41.67, 41.48; **H, 3.89, 3.92.**

Upon catalytic hydrogenation, in the presence of platinum, the nitroacetate takes up approximately **2.5** moles of hydrogen. We have not yet studied the reactions of the reduced product.

This intermediate nitroacetate does not give an enol test with ferric chloride solution and does not decolorize a solution of bromine in carbon tetrachloride at 20°. The nitro-acetate shows the characteristic reducing action of aldehydes, with Fehling's solution and with ammoniacal silver oxide. It is decomposed on heating with water; on warming with pyridine it is converted almost quantitatively, by an ***endothermzc*** reaction, into methyl 5-nitrofuroate. The latter, after one crystallization from methyl alcohol, formed colorless crystals, m. p. 81.6° (corr.). This product is evidently purer than that obtained by Marquis, who reported a melting-point of 78.5°.

In addition to the crystalline nitroacetate described above, there was obtained an almost equal quantity of a heavy yellow oil, which was obtained from the crystals by pressing on a suction filter and by adding water to the mother liquors from the crystallization of the solid nitroacetate. This oil was dissolved in ether, washed free from acid by means of cold sodium bicarbonate solution, and finally freed from alkali by repeated washing with cold water. The ether solution was allowed to stand at 0° for several days in order to separate an additional quantity of the crystals. After filtering these off and evaporating off the solvent under reduced pressure, there remained a yellow viscous oil from which no further quantity of crystals could be separated. On warming the oil with pyridine, a violent ***exothermic*** reaction occurs and the solution becomes very deeply colored (almost black). On pouring this into water, a highly colored insoluble precipitate is formed, from which only 25–30% of the calculated quantity of methyl 5-nitrofuroate could be isolated. The fact that a violent exothermic reaction occurs on

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[7] **Dennis and Shelton,** THIS JOURNAL, 52, 3128 **(1930).**

treatment with pyridine, indicates that the oil contains a substance more reactive than the crystalline nitroacetate. The formation of methyl 5-nitrofuroate may be due to the presence of the crystalline nitroacetate dissolved in the oil.

Decarboxylation of 5-Nitrofuroic Acid: 2-Nitrofuran.—Five grams of the pure dry acid (m. p. 185–185.5°), 10 g. of high-boiling coal tar bases (b. p. 145–165° at 15 mm.) and 1 g. of copper–bronze (Kahlbaum's Naturkupfer C) were placed in a Wood's metal bath at 160–180°, and the temperature was finally raised to 220" after the original vigorous decomposition had subsided. The procedure was similar to that used for the decarboxylation of the halogenated furoic acids.[8] The distillates from several runs were combined and subjected to steam distillation. The volatile products were extracted with ether and the extract was washed thrice with cold dilute hydrochloric acid to remove any bases. After washing with cold water until the washings were free from acid, the ether solution was dried over anhydrous sodium sulfate. After removal of the solvent under diminished pressure, the residual crude 2-nitrofuran was dissolved in the minimum amount of petroleum benzine (b. p. 60–70°) at 50°. The warm solution was decanted from a small tarry residue and cooled to 0°, with vigorous stirring. The faintly pink crystals of 2-nitrofuran were filtered with suction, washed with a little of the cold solvent and then recrystallized in the same manner. The purified 2-nitrofuran formed almost colorless crystals melting at 28.8–29.2° (corr.). From 27 g. of 5-nitrofuroic acid there was obtained 2.8 g. of 2-nitrofuran (14% yield).

Nitration of Furan: 2-Nitrofuran.—The nitration of furan was carried out in acetic anhydride, according to the procedure of Marquis. After several crystallizations from petroleum benzine (b. p. 60–70°), the product formed pale yellow crystals, m. p. 28.8-29.2' (corr.). The identity of this nitrofuran with the specimen of 2-nitrofuran resulting from the decarboxylation of 5-nitrofuroic acid was established by a microscopical examination of the crystals and a mixed melting point determination. A mixture of the two substances in equal amounts melted at 28.8–29.2" (corr.), which is the melting point of the original pure substances.

Microscopical Examination of **2-Nitrofuran.**[9]—Two samples of this compound, one prepared by the direct nitration of furan and the other by nitration of furoic acid and subsequent decarboxylation, exhibited exactly the same optical properties.

2-Nitrofuran was found to be very soluble in xylene at room temperature but it yielded well formed crystals from this solvent when cooled to 0°. With this treatment, long, slender prisms were obtained as well as some smaller parallelograms. Both the prisms and the parallelograms were of two types, which will be designated as "type A" and "type B." Type A crystals were rectangular in shape, varying in length from squares to long prisms. In these, extinction was parallel. Type B crystals were parallelograms having an acute angle of about 68°. These, also, varied greatly in length. In this type, extinction was oblique to the direction of elongation and parallel to the shorter side. It was evident that the prisms were merely elongations of the shorter types. Type B crystals of both samples showed a marked tendency to form twins on the longer

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[8] Shepard, Winslow and Johnson, THIS JOURNAL, 52,2083 (1930).

[9] The authors are indebted to Mr. P. P. McClellan for carrying out this microscopical examination.

side. Interference figures indicated that the crystals were biaxial, hence they must belong to the monoclinic system. The trace of the optic plane was parallel to the shorter side of type B crystals.

Summary

2-Nitrofuran has been prepared by the decarboxylation of 5-nitrofuroic acid and has been shown to be identical with the nitrofuran obtained from furan by nitration. The latter had been incorrectly formulated by Marquis to be 3-nitrofuran.

Evidence is presented to support the view that the intermediate nitroacetates, produced in the nitration of various furan derivatives in acetic anhydride solution, are ring structures rather than open chain enols.

The mechanism of the nitration process is suggested tentatively to be a 1,4-addition to the furan ring, without scission of the oxygen bridge.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE ACTION OF PHENOL ON BENZOYLDIPHENYLMETHYL BROMIDE

BY C. FREDERICK KOELSCH[1]

RECEIVED JANUARY 21, 1931 PUBLISHED MARCH 6, 1931

In a recent paper Schuster[2] reported that the reaction between benzoyldiphenylmethyl bromide and phenol gave phenylbenzoin monophenyl ether

$$(C_6H_5)_2CBrCOC_6H_5 + C_6H_5OH \longrightarrow HBr + \underset{(I)}{(C_6H_5)_2C(OC_6H_5)COC_6H_5} \qquad (1)$$

Subsequent treatment of the resulting product with phenylmagnesium bromide was reported to give benzopinacone monophenyl ether

$$(C_6H_5)_2C(OC_6H_5)COC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_2C(OC_6H_5)C(OH)(C_6H_5)_2 \qquad (2)$$

A reaction such as that indicated in (1) would be remarkable indeed, since it is well known that phenol reacts in an acidic environment with certain compounds containing labile halogens to form nuclear substitution products; for example, phenol and triphenylchloromethane form *p*-hydroxytetraphenylmethane. It was then supposed that reaction (1) did not proceed as Schuster indicated, but rather

$$(C_6H_5)_2CBrCOC_6H_5 + C_6H_5OH \ \_\quad HBr + \underset{(II)}{(C_6H_5)_2C(C_6H_4OH)COC_6H_5} \qquad (3)$$

To test this supposition, Schuster's work was repeated in this Laboratory.

In the present paper it is shown that the reaction between benzoyldiphenylmethyl bromide and phenol proceeds neither according to (1) nor

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[1] Du Pont Fellow, 1930–1931.

[2] Schuster, *Ber.*, 63, 2397 (1930).

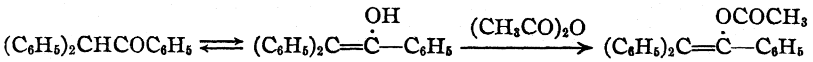
according to (3). Instead, it is shown that the reaction takes place in the following manner

$$(C_6H_5)_2CBrCOC_6H_5 + C_6H_5OH \longrightarrow \underset{\text{(III)}}{(C_6H_5)_2CHCOC_6H_5} + p\text{-}BrC_6H_4OH \qquad (4)$$

The first evidence that diphenylacetophenone (III) and not phenylbenzoin monophenyl ether (I) or hydroxytriphenylacetophenone (II) was produced in the reaction was obtained by treating the product with alcoholic potassium hydroxide, when potassium benzoate and diphenylmethane were formed

$$(C_6H_5)_2CHCOC_6H_5 + KOH \longrightarrow (C_6H_5)_2CH_2 + C_6H_5COOK$$

Later, it was found that the product, when treated with acetic anhydride and sulfuric acid, gave triphenylvinyl acetate



$$(C_6H_5)_2CHCOC_6H_5 \rightleftarrows (C_6H_5)_2C{=}\overset{OH}{\dot{C}}{-}C_6H_5 \xrightarrow{(CH_3CO)_2O} (C_6H_5)_2C{=}\overset{OCOCH_3}{\dot{C}}{-}C_6H_5$$

Finally, the identity of the product was proved by determining its melting point when mixed with a known specimen of diphenylacetophenone which had been prepared by the reactions[3]

$$C_6H_5CH(OH)COOCH_3 + C_6H_5MgBr \longrightarrow C_6H_5CH(OH)C(C_6H_5)_2OH \xrightarrow{-H_2O} C_6H_5COCH(C_6H_5)_2$$

Further evidence that the reaction proceeds according to Equation 4 was obtained by the isolation of *p*-bromophenol in considerable amounts from the reaction mixture. This compound was identified beyond question by its boiling point and by the melting point and neutral equivalent of the aryloxyacetic acid obtained from it by treatment with chloroacetic acid and sodium hydroxide.

The product of the action of phenylmagnesium bromide on diphenylacetophenone, which melts at 232–233' and not at 219° as Schuster reported, is a,α,β,β-tetraphenylethanol[4]

$$(C_6H_5)_2CHCOC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_2CHC(C_6H_5)_2OH$$

On treatment with alcoholic potassium hydroxide it gave a mixture of diphenylmethane and benzophenone

$$(C_6H_5)_2CHC(C_6H_5)_2OH \longrightarrow (C_6H_5)_2CH_2 + (C_6H_5)_2CO$$

Schuster noted and was unable to explain the resistance of the hydroxyl group to substitution by bromine on treatment with hydrogen bromide in the compound which he obtained by the action of phenylmagnesium bromide on his supposed phenylbenzoin monophenyl ether. Since it has been pointed out that this reaction product is really α,α,β,β-tetraphenylethanol, and since unreactivity toward such a reagent as hydrogen bromide is apparently a characteristic property of polyphenylethanols,[5] this behavior of the compound in question is not surprising.

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[3] Orekhoff, *Bull. soc. chim.*, [4] 25, 189 (1919).

[4] McKenzie and Boyle, J. *Chem. Soc.*, 119, 1140 (1921).

[5] *Cf.* Schmidlin, *Ber.*, 43, 1146 (1910)

Experimental

Benzoyldiphenylmethyl Bromide and Phenol.—The procedure of Schuster for carrying out the reaction between these two compounds was followed closely. Eight grams of benzoyldiphenylmethyl bromide[6] was heated at 100° for three hours with 3.2 g. of phenol. The product, after triturating with dilute sodium hydroxide solution, was crystallized from alcohol, giving 5.25 g. of diphenylacetophenone melting at 135–136°, uncorr. (On heating with concentrated sulfuric acid, diphenylacetophenone gives a deep green solution. The color becomes reddish-brown on dilution.)

The oil obtained on acidification of the sodium hydroxide extract was taken up in ether, dried, and the ether removed. Distillation of the residue at 23 mm. gave two main fractions, both of which solidified. The first (1.2 g.), which boiled at 80–85°, was phenol; the second (1.9 g.), which boiled at 127–130°, was identified as *p*-bromophenol by the preparation of p-bromophenoxyacetic acid from it, which melted at 156–158° and had a neutral equivalent of 228.[7]

Cleavage of Diphenylacetophenone by Potassium Hydroxide.—Three grams of the ketone obtained above was refluxed for twenty hours with a solution of 2 g. of potassium hydroxide in 50 ml. of alcohol. The solvent was removed in a current of air at reduced pressure, water was added, and the mixture was steam distilled. From the distillate was obtained 1.6 g. of diphenylmethane boiling at 145–150° at 25 mm., and melting at 21–23", which gave benzophenone on oxidation with chromic acid. The residue from the steam distillation gave on acidification 1.02 g. of benzoic acid melting at 120–121°; neutral equivalent, 120.

Triphenylvinyl Acetate.—A mixture of 0.5 g. of diphenylacetophenone with 5 ml. of acetic anhydride and 3 drops of concentrated sulfuric acid was heated at 60–70° for twelve hours. The product, on crystallization from dilute acetic acid, melted at 102–104°,[8] and gave diphenylacetophenone on warming with alcoholic sodium hydroxide.

Only unchanged diphenylacetophenone was recovered when an attempt was made to methylate the compound with dimethyl sulfate and alkali in methyl alcohol.

α,α,β,β-Tetraphenylethanol.—To the filtered solution of phenylmagnesium bromide prepared from 20 g. of phenyl bromide in 50 ml. of ether was added 8 g. of diphenylacetophenone. The solution, after refluxing for half an hour, was worked up as described by Schuster, giving a product which on one crystallization from toluene melted at 218–223°. On repeated recrystallization from toluene, this was separated into *α,α,β,β*-tetraphenylethanol melting at 227–229° uncorr. (2.4 g.), and unchanged diphenylacetophenone (4.6 g.).[4]

Cleavage of *α,α,β,β*-Tetraphenylethanol by Potassium Hydroxide.—One gram of the alcohol was refluxed for two hours with 1 g. of potassium hydroxide dissolved in 20 tnl. of alcohol. Water was added after removing the alcohol under reduced pressure, and the mixture was steam distilled. The residue contained only a negligible amount of organic material. The oil in the distillate was taken up in ether; this solution was dried with calcium chloride and treated with the filtered Grignard solution from 3.0 g. of phenyl bromide. Dilute sulfuric acid was added, the ether was removed, and the residue was steam distilled. The distillate contained 0.27 g. of diphenylmethane (calcd. 0.48 g.) identified by oxidation to benzophenone. The non-volatile organic substance was identified as triphenylcarbinol by its melting point (159–160°, uncorr.) and its characteristic color reaction with concentrated sulfuric acid; it weighed 0.65 g., correspondimg to 0.45 g. of benzophenone (calcd. 0.52 g.).

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[6] Lowenbein and Schuster, *Ann.*, 481, 106 (1930).

[7] Koelsch, THIS JOURNAL, 53, 305 (1931).

[8] Biltz, Ann., 296, 245 (1897).

The assistance of Professor S. M. McElvain is gratefully acknowledged.

Summary

The reaction between phenol and benzoyldiphenylmethyl bromide gives p-bromophenol and diphenylacetophenone.

The compounds described as phenylbenzoin monophenyl ether and benzopinacone monophenyl ether by Schuster[2] are in reality diphenylacetophenone and $\alpha,\alpha,\beta,\beta$-tetraphenylethanol.

Diphenylacetophenone and $\alpha,\alpha,\beta,\beta$-tetraphenylethanol are smoothly cleaved by alcoholic potassium hydroxide, giving in the one case benzoic acid and diphenylmethane, and in the other benzophenone and diphenylmethane.

MADISON, WISCONSIN

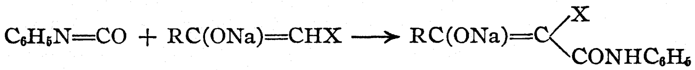
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE COURSE OF ADDITION OF SODIUM ENOL ALKYLMALONIC AND SODIUM ENOL ALKYLCYANACETIC ESTERS TO UNSATURATED ESTERS

BY ARTHUR MICHAEL AND JOHN ROSS

RECEIVED JANUARY 24, 1931 PUBLISHED MARCH 6, 1931

According to the law of chemical neutralization,[1] the course of an addition reaction involving the use of an enolic sodium derivative will be such as to produce a compound in which the sodium is in a better neutralized state. The attainment of the maximal heat of formation in the addition reaction depends upon the neutralization of the positive energy of the metal and this energy factor determines the utmost possible degradation of chemical energy. This generalization is well illustrated in the reactions of sodium enol derivatives with phenyl isocyanate.[2] With the sodium enol derivatives of acetoacetic, malonic, formyl, acetic, benzoylacetic esters and diacylmethane, the reaction takes place smoothly to give in most cases almost quantitative yields of anilides, thus



$$C_6H_5N{=}CO + RC(ONa){=}CHX \longrightarrow RC(ONa){=}C\begin{cases}X\\ CONHC_6H_5\end{cases}$$

I

In these derivatives the a-hydrogen atoms of the enolic sodium mother substances are replaced by the negative $—CONHC_6H_5$ group, and, hence, the sodium atoms are better neutralized in the C-addition products (I). When there is no a-hydrogen atom in the sodium compound, this simple reaction cannot take place. For example, with the sodium enol derivatives of ethylmalonic and ethylacetoacetic esters maximal possible energy degradation is attained by the phenyl isocyanate polymerizing mainly

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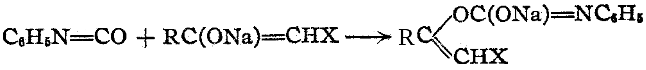
[1] Michael. J. *prakt. Chem.*, 60, 293 (1899); THIS JOURNAL, 32, 990 (1910).

[2] Michael, *Ber.*, 38, 22 (1905).

to the much less energetic isocyanurate and a small amount of the same neutral sodium product of destructive decomposition is formed from **each** sodium enolic ester.

A second course of these reactions would be the formation of sodium enol 0-addition products, that is, of sodium enolic urcthan derivatives



II

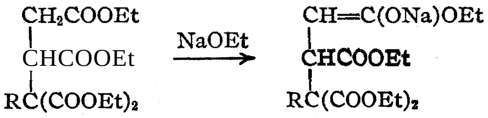
According to the law of chemical neutralization, such a procedure is not possible, since the metal in the compound (II) would be much less neutralized than in the original sodium enolates. Indeed, the tendency to form sodium enol urethans is so slight that sodium ethoxide does not unite with phenyl isocyanate, but entirely converts it into isocyanurate.

Auwers, Kobner and Meyenberg[3] showed that sodium enol alkylmalonic esters readily added to fumaric ester, and, from the addition product upon hydrolysis, obtained a-alkyl tricarballylic acids. The addition reaction was written[4]

$$\mathrm{RCNa(COOEt)_2} + \begin{matrix}\mathrm{CHCOOEt}\\ \| \\ \mathrm{CHCOOEt}\end{matrix} \longrightarrow \begin{matrix}\mathrm{CHNaCOOEt}\\ | \\ \mathrm{CHCOOEt}\\ | \\ \mathrm{RC(COOEt)_2}\end{matrix}$$

III

Since Michael[5] showed that the addition products of sodium enol methylmalonic ester and sodium enol ethylmalonic ester with fumaric ester readily gave sodium derivatives, which could be methylated upon treatment with methyl iodide, it was apparent that the original addition compound could not be a y-alkyl y-carbethoxy tricarballylic ester (111), unless such an ester formed a stable sodium derivative (IV) at the α-carbethoxy group



$$\begin{matrix}\mathrm{CH_2COOEt}\\ | \\ \mathrm{CHCOOEt}\\ | \\ \mathrm{RC(COOEt)_2}\end{matrix} \xrightarrow{\mathrm{NaOEt}} \begin{matrix}\mathrm{CH{=}C(ONa)OEt}\\ | \\ \mathrm{CHCOOEt}\\ | \\ \mathrm{RC(COOEt)_2}\end{matrix}$$

III IV

Michael concluded from his experiments that these esters gave stable enolic sodium derivatives (IV), but the recent examination of such addition reactions with α,β-unsaturated, monobasic olefinic esters[6] made it probable that the alkyl group migrated in the addition of sodium enol alkylmalonic esters to the unsaturated dibasic ester, thus forming compounds containing a malonic ester residue that would give stable sodium

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[3] Auwers, Kobner and Meyenberg, *Ber.*, 24,2890 (1891).

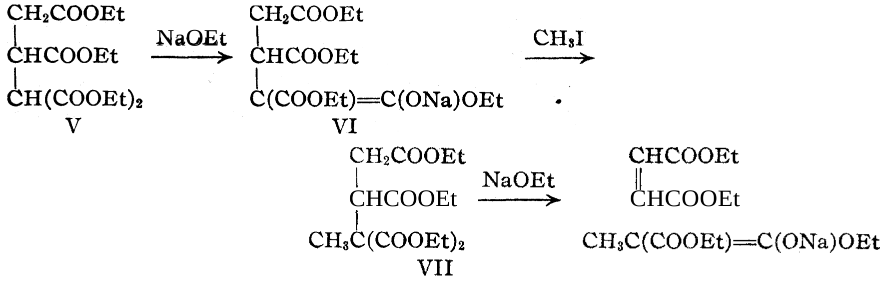
[4] Ethyl is more conveniently represented by Et throughout this paper.

[5] Michael, *Ber.*, **33**, 3731 (1900).

[6] Michael and Ross, THIS JOURNAL, 52,4598 (1930).

enol derivatives and could therefore be alkylated. In order to ascertain whether this had occurred, these reactions were re-examined.

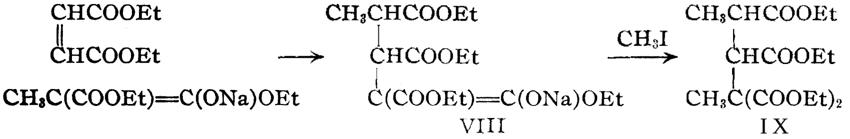
Butane α,β,γ,γ-tetracarboxylic ester (VII) was prepared by methylation of the sodium derivative of propane α,β,γ,γ-tetracarboxylic ester (VI). Upon treatment with anhydrous sodium ethoxide, in ether at 0°, followed by methyl iodide, the butane derivative (VII) mainly underwent retrogression to form fumaric ester and sodium enol methylmalonic ester



$$\begin{array}{l} CH_2COOEt \\ | \\ CHCOOEt \\ | \\ CH(COOEt)_2 \\ \text{V} \end{array} \xrightarrow{NaOEt} \begin{array}{l} CH_2COOEt \\ | \\ CHCOOEt \\ | \\ C(COOEt){=}C(ONa)OEt \\ \text{VI} \end{array} \xrightarrow{CH_3I}$$

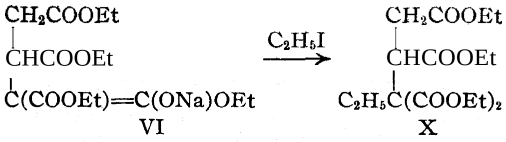
$$\begin{array}{l} CH_2COOEt \\ | \\ CHCOOEt \\ | \\ CH_3C(COOEt)_2 \\ \text{VII} \end{array} \xrightarrow{NaOEt} \begin{array}{l} CHCOOEt \\ \| \\ CHCOOEt \\ \\ CH_3C(COOEt){=}C(ONa)OEt \end{array}$$

The sodium enol methylmalonic ester thus formed was converted by the methyl iodide into dimethylmalonic ester. This course of the reaction is in marked contrast to that of the addition product of sodium enol methylmalonic and fumaric esters, which under parallel conditions methylate to give a quantitative yield of α,γ-dimethyl γ-carbethoxytricarballylic ester (IX).[7] The first addition reaction therefore takes place with migration of methyl, *i. e.*



$$\begin{array}{l} CHCOOEt \\ \| \\ CHCOOEt \\ \\ CH_3C(COOEt){=}C(ONa)OEt \end{array} \longrightarrow \begin{array}{l} CH_3CHCOOEt \\ | \\ CHCOOEt \\ | \\ C(COOEt){=}C(ONa)OEt \\ \text{VIII} \end{array} \xrightarrow{CH_3I} \begin{array}{l} CH_3CHCOOEt \\ | \\ CHCOOEt \\ | \\ CH_3C(COOEt)_2 \\ \text{IX} \end{array}$$

It was further shown that pentane α,β,γ,γ-tetracarboxylic ester (X) prepared by action of ethyl iodide upon the sodium derivative of propane α,β,γ,γ-tetracarboxylic ester (VI) remained unchanged upon treatment in the cold with sodium ethoxide and methyl iodide



$$\begin{array}{l} CH_2COOEt \\ | \\ CHCOOEt \\ | \\ C(COOEt){=}C(ONa)OEt \\ \text{VI} \end{array} \xrightarrow{C_2H_5I} \begin{array}{l} CH_2COOEt \\ | \\ CHCOOEt \\ | \\ C_2H_5C(COOEt)_2 \\ \text{X} \end{array}$$

Upon treatment of the addition product of sodium enol ethylmalonic ester to fumaric ester in the cold with sodium ethoxide and methyl iodide, the tetracarboxylic ester is methylated with facility.[8] It therefore follows

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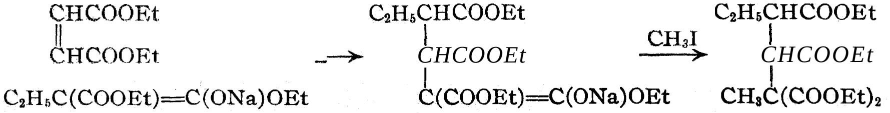
[7] Michael, Ref. 5, p. 3763.

[8] Michael, *ibid.*, p. 3746.

that in the latter addition reaction the ethyl group has migrated to the a-position, thus

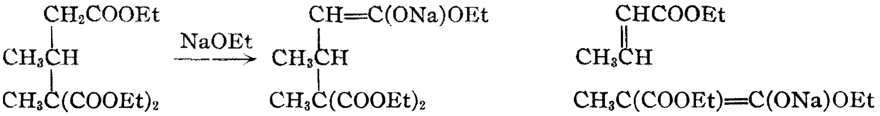


$$\begin{array}{l}\mathrm{CHCOOEt}\\ \| \\ \mathrm{CHCOOEt}\\ \\ \mathrm{C_2H_5C(COOEt){=}C(ONa)OEt}\end{array} \longrightarrow \begin{array}{l}\mathrm{C_2H_5CHCOOEt}\\ | \\ \mathit{CHCOOEt}\\ | \\ \mathrm{C(COOEt){=}C(ONa)OEt}\end{array} \xrightarrow{\mathrm{CH_3I}} \begin{array}{l}\mathrm{C_2H_5CHCOOEt}\\ | \\ \mathit{CHCOOEt}\\ | \\ \mathrm{CH_3C(COOEt)_2}\end{array}$$

XI XII

The retrogression reaction that occurred when the free esters from the addition products of sodium enol alkylmalonic esters to crotonic ester were treated with sodium[9] was later shown by Ingold[10] and Kohler and Butler[11] to take place by the action of sodium ethoxide upon similar addition products. Ingold considered that such reversal of the additive process indicated that the additive process itself was a balanced reaction which proceeded until a definite equilibrium was attained under the conditions in which the reaction was carried out. The following view offers an insight into the mechanism of the retrogression reaction.

Michael[12] explained the formation of acetoacetic ester from ethyl acetate and sodium through the primary formation of $CH_2{=}C(ONa)OEt$ and Scheibler and Marhenkel[13] on isolating this compound, proved the correctness of this view. It therefore seemed probable that the capacity of the ester (XIII) to form a sodium derivative at the α-carbethoxyl group as in (XIV) was due to the near spatial negative influence of the four oxygen atoms upon the C and H_2 of the CH2 group. However, the strong positive influence of the sodium introduced into ester (XIII) must decrease the affinity for each other of the two C atoms of (XIV) attached to the methyl groups, and the very considerable positive free chemical energy of the sodium in (XIV) is able to attain a much better neutralization by the retrogression of (XIV) into sodium enol malonic and crotonic esters.



$$\begin{array}{l}\mathrm{CH_2COOEt}\\ | \\ \mathrm{CH_3CH}\\ | \\ \mathrm{CH_3C(COOEt)_2}\end{array} \xrightarrow{\mathrm{NaOEt}} \begin{array}{l}\mathrm{CH{=}C(ONa)OEt}\\ | \\ \mathrm{CH_3CH}\\ | \\ \mathrm{CH_3C(COOEt)_2}\end{array} \qquad \begin{array}{l}\mathrm{CHCOOEt}\\ \| \\ \mathrm{CH_3CH}\\ \\ \mathrm{CH_3C(COOEt){=}C(ONa)OEt}\end{array}$$

XIII XIV

The intermediate formation of such a sodium derivative as (XIV) is, therefore, not improbable.

That pentane α,β,y,y-tetracarboxylic ester (X) did not undergo retrogression upon treatment with sodium ethoxide and methyl iodide may have been due to incapacity to form such a sodium derivative as in

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[9] Michael, Ref. 5, p. 3749.

[10] Ingold, J. *Chem. Soc.*, 119, 1976 (1921).

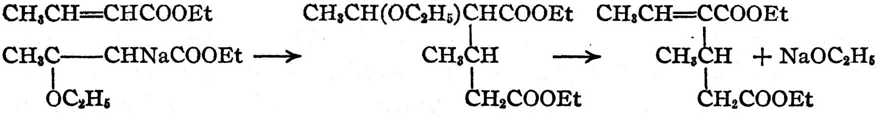
[11] Kohler *and* Butler, THIS JOURNAL, 48, 1040 (1926).

[12] Michael, Ber., 38, 1933 (1905).

[13] Scheibler *and* Marhenkel. Ann., 458, 1 (1927).

(XIV), owing to the influence of the more positive character of the ethyl compared with the methyl group.

It was thought that separation of the ethyl group from the directly attached carbon atom of sodium enol ethylmalonic ester would not take place as readily as the separation of the methyl group of sodium enol methylmalonic ester, and that the difference might be reflected in the yields of addition product obtained. The reaction between sodium enol ethylmalonic and crotonic ester was therefore examined. Contrary to the behavior of sodium enol methylmalonic ester,[6] only slight addition was found to occur; the crotonic ester mainly polymerized to the sodium derivative of a dimeric ester, a-ethylidene β-methylglutaric ester (XV) which v. Pechmann[14] had obtained by the action of sodium ethoxide, and Michael[15] by the action of sodium on crotonic ester. This reaction was expressed by v. Pechmann as follows[16]



$$\begin{array}{l} \mathrm{CH_3CH{=}CHCOOEt} \\ \mathrm{CH_3\underset{\displaystyle OC_2H_5}{\underset{|}{C}}{-\!-}CHNaCOOEt} \longrightarrow \end{array} \begin{array}{c} \mathrm{CH_3CH(OC_2H_5)CHCOOEt} \\ | \\ \mathrm{CH_3CH} \\ | \\ \mathrm{CH_2COOEt} \end{array} \longrightarrow \begin{array}{c} \mathrm{CH_3CH{=}CCOOEt} \\ | \\ \mathrm{CH_3CH} \\ | \\ \mathrm{CH_2COOEt} \end{array} + \mathrm{NaOC_2H_5}$$

XV

The fact that the sodium derivative of enol ethylmalonic ester causes the polymerization of crotonic ester while that of methylmalonic ester does not, is to be attributed to the more energetic state of the metal in the first ester. Addition of sodium enol ethylmalonic ester to crotonic ester would require the migration of the ethyl group, and apparently polymerization of the crotonic ester takes place more readily.

Since no addition product was obtained in the above reaction, attention was directed to the ease of migration of alkyl groups during the addition of sodium enol alkyl cyanacetic esters to unsaturated esters. J. F.

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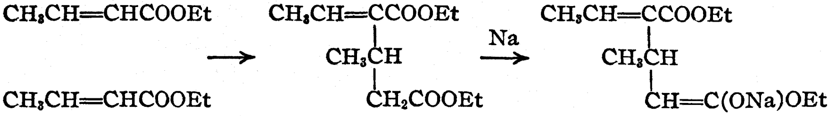
[14] V. Pechmann, Ber., 33, 3340 (1900).

[15] Michael, ibid., 33, 3760 (1900).

[16] There is no evidence that crotonic ester unites with sodium ethylate and the existence of the assumed sodium β-ethoxybutyric ester is improbable, apart from the assumption of the direct union of sodium with carbon. The assumed intermediate stage is therefore untenable as is also the last step. since Michael showed that the sodium derivative of the dimeric crotonic ester appears as the final reaction product. The reaction represents a polymerization by addition, resulting in the better neutralization of the sodium



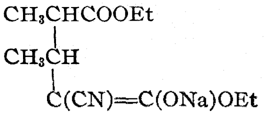
$$\begin{array}{l} \mathrm{CH_3CH{=}CHCOOEt} \\ \\ \\ \\ \mathrm{CH_3CH{=}CHCOOEt} \end{array} \longrightarrow \begin{array}{c} \mathrm{CH_3CH{=}CCOOEt} \\ | \\ \mathrm{CH_3CH} \\ | \\ \mathrm{CH_2COOEt} \end{array} \xrightarrow{\mathrm{Na}} \begin{array}{c} \mathrm{CH_3CH{=}CCOOEt} \\ | \\ \mathrm{CH_3CH} \\ | \\ \mathrm{CH{=}C(ONa)OEt} \end{array}$$

Although the sodium addition product contains the group $—\mathrm{CH{=}C(ONa)OEt}$, it does not suffer retrogression because crotonic ester does not give a sodium derivative. This is an interesting point in support of the theoretical views upon the retrogression reaction discussed above.

Thorpe[17] concluded that in the addition of sodium enol a-cyano propionic ester to β,β-dimethylacrylic ester, the parts of the addendum appeared to be CH_3 and —C(CN)=C(ONa)OEt. Upon examination of the addition of sodium enol α-cyanopropionic ester to crotonic ester, it was found that addition also occurred with migration of the methyl radical to the a-C atom of the latter ester, that is, the addendum functioned as CH_3 and —C(CN)=C(ONa)OEt

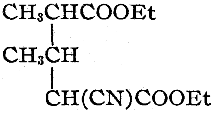
$CH_3CH{=}CHCOOEt$

$CH_3C(CN){=}C(ONa)OEt$



$$\begin{array}{l} CH_3CHCOOEt \\ \quad | \\ CH_3CH \\ \quad | \\ \quad C(CN){=}C(ONa)OEt \end{array}$$

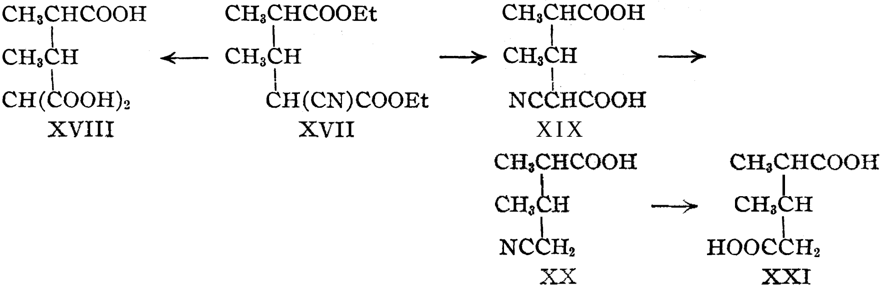
XVI



$$\begin{array}{l} CH_3CHCOOEt \\ \quad | \\ CH_3CH \\ \quad | \\ \quad CH(CN)COOEt \end{array}$$

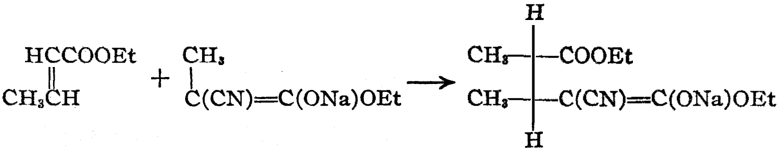
XVII

The product, α,β-dimethyl γ-cyanoglutaric ester (XVII), is apparently a stereomeric form of the cyano ester obtained by the addition of sodium enol cyanacetic ester to tiglic ester.[6] Upon saponification (XVII) gave a sirupy cyano acid (XIX) which upon treatment with hydrochloric acid gave very little α,β-dimethylglutarimide, but mainly a liquid cyano acid (XX). This was converted into trans α,β-dimethylglutaric acid, which was identified by its di-anilide. Hydrolysis of the cyano ester gave a tricarboxylic acid (XVIII), which was not identical with the corresponding acid prepared through the addition of sodium enol cyanacetic ester to tiglic ester, and was therefore apparently a stereomer of that acid



$$\begin{array}{lcllcl} \begin{array}{l} CH_3CHCOOH \\ \quad | \\ CH_3CH \\ \quad | \\ CH(COOH)_2 \end{array} & \longleftarrow & \begin{array}{l} CH_3CHCOOEt \\ \quad | \\ CH_3CH \\ \quad | \\ \quad CH(CN)COOEt \end{array} & \longrightarrow & \begin{array}{l} CH_3CHCOOH \\ \quad | \\ CH_3CH \\ \quad | \\ NCCHCOOH \end{array} & \longrightarrow \\ \text{XVIII} & & \text{XVII} & & \text{XIX} & \\ & & & & \begin{array}{l} CH_3CHCOOH \\ \quad | \\ CH_3CH \\ \quad | \\ NCCH_2 \end{array} \; \longrightarrow & \begin{array}{l} CH_3CHCOOH \\ \quad | \\ CH_3CH \\ \quad | \\ HOOCCH_2 \end{array} \\ & & & & \text{XX} & \text{XXI} \end{array}$$

Considering the addition reaction in each case to take place as a *trans* process,[18] the following stereomeric compounds would be expected to be formed



$$\begin{array}{l} HCCOOEt \\ \quad \| \\ CH_3CH \end{array} + \begin{array}{l} CH_3 \\ | \\ C(CN){=}C(ONa)OEt \end{array} \longrightarrow \begin{array}{c} H \\ | \\ CH_3{-}|{-}COOEt \\ CH_3{-}|{-}C(CN){=}C(ONa)OEt \\ | \\ H \end{array}$$

XXII

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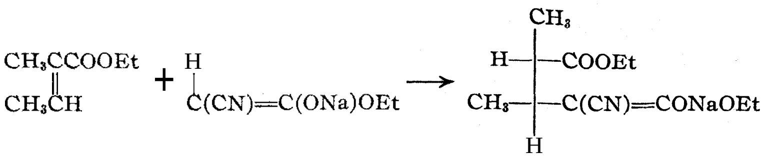
[17] J. F. Thorpe, J. *Chem. Soc.*, 77,923 (1900).

[18] See Michael, J. *prakt. Chem.*, 52,289 (1895); THIS JOURNAL, 40, 1674 (1918).

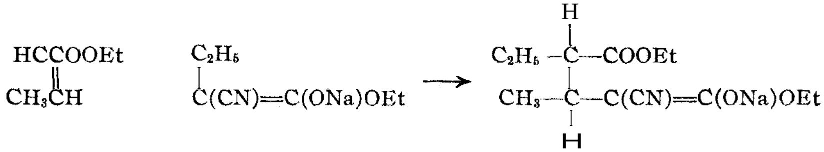


$$\begin{array}{l}CH_3CCOOEt\\ \quad\|\\ CH_3CH\end{array} + \begin{array}{l}H\\ |\\ C(CN){=}C(ONa)OEt\end{array} \longrightarrow \begin{array}{c}CH_3\\ |\\ H{-}|{-}COOEt\\ CH_3{-}|{-}C(CN){=}CONaOEt\\ |\\ H\end{array}$$

XXIII

It agrees with this interpretation, that the addition of sodium enol cyanacetic ester to tiglic ester gave a cyano ester stereomeric with the product of addition of sodium enol a-cyanopropionic ester to crotonic ester.

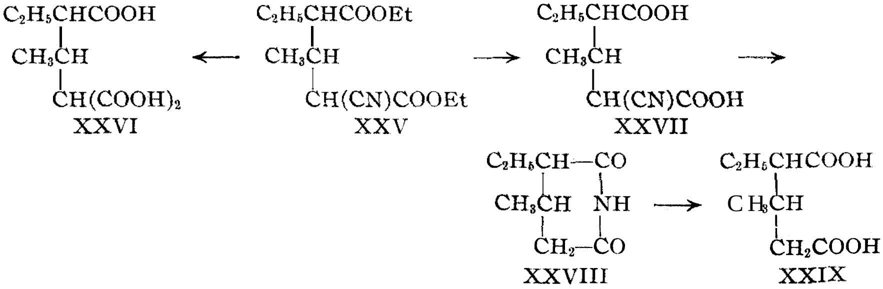
Results parallel to those with sodium enol a-cyanopropionic ester were obtained in the addition of sodium enol a-cyanobutyric ester to crotonic ester. A 33% yield of a-ethyl-B-methyl-y-cyanoglutaric ester (XXV) was obtained from the addition product (XXIV), showing that the parts of the addendum were C_2H_5 and C(CN)=C(ONa)OEt. With *trans* addition the reaction proceeds as follows



$$\begin{array}{l}HCCOOEt\\ \quad\|\\ CH_3CH\end{array} \quad \begin{array}{l}C_2H_5\\ |\\ C(CN){=}C(ONa)OEt\end{array} \longrightarrow \begin{array}{c}H\\ |\\ C_2H_5{-}C{-}COOEt\\ |\\ CH_3{-}C{-}C(CN){=}C(ONa)OEt\\ |\\ H\end{array}$$

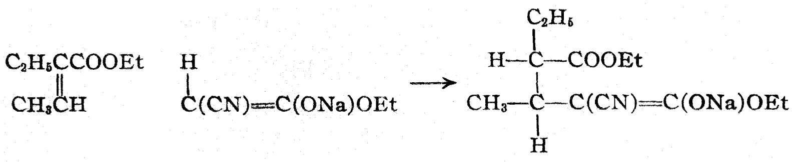
XXIV

Upon saponification of the ester (XXV), a cyano acid (XXVII) melting at 147° was obtained, which upon treatment with hydrochloric acid was almost completely converted into α-ethyl-β-methylglutarimide, m. p. 92°, together with a small amount of a stereomeric imide, m. p. 102°. Since both imides gave the same *cis* α-ethyl-β-methylglutaric acid, m. p. 88° (XXIX), upon hydrolysis, it is considered that they are related to one another as *cis* and *trans* with respect to the methyl and ethyl groups and the plane of the imide ring. Through saponification with caustic potash, the ester (XXV) gave α-ethyl-β-methyl-γ-carboxyglutaric acid (XXVI), melting at 143°. These reactions are represented by



$$\underset{XXVI}{\begin{array}{l}C_2H_5CHCOOH\\ CH_3CH\\ CH(COOH)_2\end{array}} \longleftarrow \underset{XXV}{\begin{array}{l}C_2H_5CHCOOEt\\ CH_3CH\\ CH(CN)COOEt\end{array}} \longrightarrow \underset{XXVII}{\begin{array}{l}C_2H_5CHCOOH\\ CH_3CH\\ CH(CN)COOH\end{array}} \longrightarrow \underset{XXVIII}{\begin{array}{l}C_2H_5CH{-}CO\\ CH_3CH\quad NH\\ CH_2{-}CO\end{array}} \longrightarrow \underset{XXIX}{\begin{array}{l}C_2H_5CHCOOH\\ CH_3CH\\ CH_2COOH\end{array}}$$

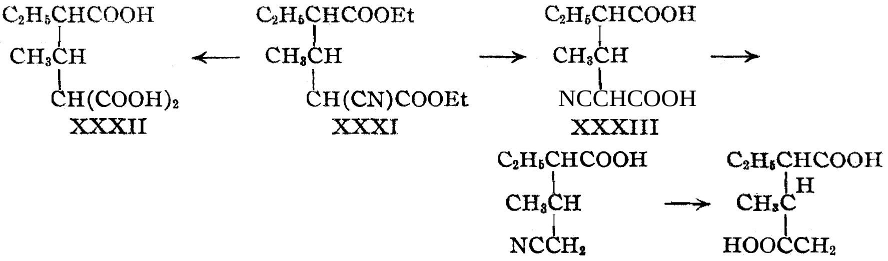
Addition of sodium enol cyanacetic ester to a-ethylcrotonic ester gave a stereomeric form (XXX) of the sodium derivative of the ester (XXIV)



$$\begin{array}{l}C_2H_5CCOOEt\\ \quad\| \\ CH_3CH\end{array} \quad \begin{array}{l}H\\ | \\ C(CN){=}C(ONa)OEt\end{array} \longrightarrow \begin{array}{l} \qquad\;\; C_2H_5 \\ \qquad\quad | \\ \quad H-C-COOEt \\ \qquad\quad | \\ CH_3-C-C(CN){=}C(ONa)OEt \\ \qquad\quad | \\ \qquad\quad H\end{array}$$

XXX

Through saponification with alcoholic potash, the ester from (XXX) yielded a cyano acid, m. p. 132° (XXXIII), and complete hydrolysis led to a tricarboxylic acid (XXXII), melting at 141°. When boiled for thirty minutes with hydrochloric acid, the cyano acid (XXXIII) gave a very small amount of the imide (XXVIII) melting at 92° with a sirupy cyano acid (XXXIV) as the main product. The latter, when completely hydrolyzed, gave trans α-ethyl-β-methylglutaric acid, m. p. 101°



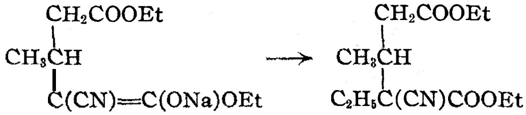
$$\begin{array}{l}C_2H_5CHCOOH\\ \quad | \\ CH_3CH \\ \quad | \\ \quad CH(COOH)_2\end{array} \longleftarrow \begin{array}{l}C_2H_5CHCOOEt\\ \quad | \\ CH_3CH \\ \quad | \\ \quad CH(CN)COOEt\end{array} \longrightarrow \begin{array}{l}C_2H_5CHCOOH\\ \quad | \\ CH_3CH \\ \quad | \\ NCCHCOOH\end{array} \longrightarrow$$

XXXII XXXI XXXIII

$$\begin{array}{l}C_2H_5CHCOOH\\ \quad | \\ CH_3CH \\ \quad | \\ NCCH_2\end{array} \longrightarrow \begin{array}{l}C_2H_5CHCOOH\\ \quad |\,H \\ CH_3C \\ \quad | \\ HOOCCH_2\end{array}$$

XXXIV XXXV

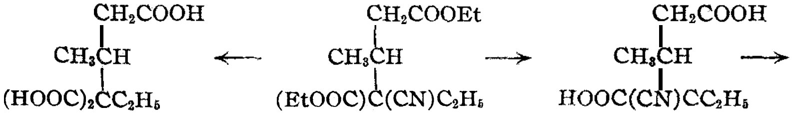
For comparison with the above compounds, β-methyl-γ-ethyl-γ-cyanoglutaric ester (XXXVII) was prepared by the action of ethyl iodide upon the sodium derivative of **β-methyl-γ-cyanoglutaric** ester (XXXVI)



$$\begin{array}{l}\quad CH_2COOEt\\ \quad | \\ CH_3CH \\ \quad | \\ \quad C(CN){=}C(ONa)OEt\end{array} \longrightarrow \begin{array}{l}\qquad CH_2COOEt\\ \qquad | \\ \quad CH_3CH \\ \qquad | \\ C_2H_5C(CN)COOEt\end{array}$$

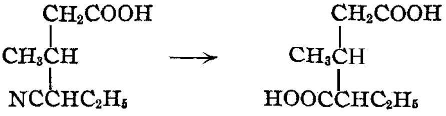
XXXVI XXXVII

From the product of saponification with caustic potash, a cyano acid (XXXIX) was obtained, melting at 139°, which upon treatment with hydrochloric acid gave a sirupy cyano acid (XL) with a very small amount of the two isomeric β-methyl-α-ethylglutarimides, m. p. 92° and m. p. 102°. Upon complete hydrolysis with hydrochloric acid, the cyano acid gave *trans* α-ethyl-β-methylglutaric acid, m. p. 101° (XLI).



$$\begin{array}{l}\qquad CH_2COOH\\ \qquad | \\ \quad CH_3CH \\ \qquad | \\ (HOOC)_2CC_2H_5\end{array} \longleftarrow \begin{array}{l}\qquad CH_2COOEt\\ \qquad | \\ \quad CH_3CH \\ \qquad | \\ (EtOOC)C(CN)C_2H_5\end{array} \longrightarrow \begin{array}{l}\qquad CH_2COOH\\ \qquad | \\ \quad CH_3CH \\ \qquad | \\ HOOC(CN)CC_2H_5\end{array} \longrightarrow$$

XXXVIII XXXVTI XXXIX



$$\begin{array}{l}CH_2COOH\\ |\\ CH_3CH\\ |\\ NCCHC_2H_5\end{array} \longrightarrow \begin{array}{l}CH_2COOH\\ |\\ CH_3CH\\ |\\ HOOCCHC_2H_5\end{array}$$

XL XLI

γ-Ethyl-β-methyl-γ-cyanoglutaric acid (XXXIX) after long boiling with 25% caustic potash, yielded the corresponding tricarboxylic acid (XXXVIII) which could not be obtained crystalline. The difficulty of hydrolysis of this substituted ethyl cyanoacetic acid is undoubtedly due to the influence of the ethyl and $—CH(CH_3)CH_2COOEt$ groups upon the cyanacetic residue. The greater stabilizing influence of the ethyl compared with the methyl group as a substituent is similarly exhibited in the difficulty of saponifying diethylmalonic ester, in comparison with the relative ease of saponification of dimethylmalonic ester.[19]

It would appear from the above reactions that addition of sodium enol cyano esters to a,@-unsaturated esters can take place with the selective synthesis of one of the stereomeric forms. It was shown above that if the primary addition reaction is considered a *trans* process then the addition of sodium enol cyanoacetic ester to a-ethylcrotonic ester would give a cyano ester stereomeric with the product of addition of sodium enol a-cyanobutyric ester to crotonic ester. When both stereomeric forms appeared, as occurred in the additions to cinnamic and a-methylcinnamic esters,[20] it is apparent that racemization had taken place during the addition reaction. This must also be the case when the same single stereomer was formed, as in the addition of sodium enol malonic to tiglic ester and of sodium enol methylmalonic to crotonic ester. McKenzie and Wren[21] and others have connected the presence of the phenyl group as favoring racemization. The action of free alkali or of sodium ethoxide in promoting racemization is well known, so that racemization would be expected to occur in the presence of a strongly alkaline material, such as sodium enol malonic ester. The absence of racemization when the sodium enol cyano esters are added to olefinic unsaturated esters is an indication of the neutrality and stability of the sodium enol cyano ester addition product in these particular cases.

In the addition of sodium enol alkyl cyanacetic esters to crotonic ester, it was noticed that always with the main product varying small quantities of higher boiling esters were formed, which gave a deep red color with alcoholic ferric chloride. Analyses indicated that they consisted of an addition product of one molecule of the alkyl cyanacetic ester to one molecule of crotonic ester. Hydrolysis with hydrochloric acid of the prod-

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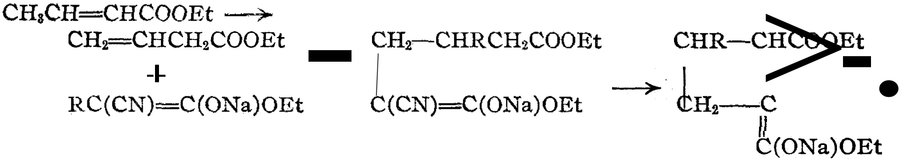
[19] Michael, *J. prakt. Chem.*, **72,** 546 **(1905).**

[20] **Ref. 6, p.** 4608.

[21] **McKenzie and Wren,** ***J. Chem. Soc.*****, 117, *680*** (1920)

uct from α-cyanopropionic and crotonic esters gave a ketone, which readily gave a semicarbazone. However, the yield of the ketone was very small, and, possibly due to the difficulty experienced in purifying this small quantity of material, the melting point and analysis of the semicarbazone did not correspond well to the expected derivative of a dimethylcyclopentanone. Notwithstanding, it was thought that this ketone might have been derived from an imino compound produced by ring-formation involving the cyano group and the H attached to the a-carbon atom.

Although crotonic ester shows no tendency to change into vinylacetic ester, yet as a hypothesis it may be supposed that in the presence of the energetic sodium enol alkyl cyanacetic ester, crotonic ester may exhibit a tendency to function in its β,γ-form



XLII XLIII

By the action of sodium ethoxide, such δ-cyano esters as (XLII) readily form sodium derivatives of cyclic imino compounds (XLIII) in which the sodium is better neutralized than in the open-chain derivatives.[22]

In a somewhat analogous case, the addition of sodium enol malonic ester to citraconic ester,[23] it has been shown[24] that, as well as the normal addition compound, a-methylpropane-a,&γ,γ-tetracarboxylic ester, there is also formed butane-α,β,δ,δ-tetracarboxylic ester, which would appear to have been produced by addition to itaconic ester. The latter tetracarboxylic ester is readily converted by sodium ethoxide into a cyclopentanone-carboxylic ester and, hence, the product of addition of sodium enol malonic ester to citraconic ester is largely the sodium derivative of this cyclic keto ester, because in this compound the sodium secures better neutralization and in the formation the maximum energy degradation is attained. To achieve this, hydrogen from the methyl group migrates during the reaction with change in the position of unsaturation so that the sitraconic ester functions during the process of addition as does itaconic ester.

The possibility indicated by the formation of high-boiling esters of an apparently cyclic structure, apparently derived from vinylacetic ester and suggesting that addition could take place at the β,γ-carbon atoms of an olefinic ester, was of sufficient interest as to warrant further examina-

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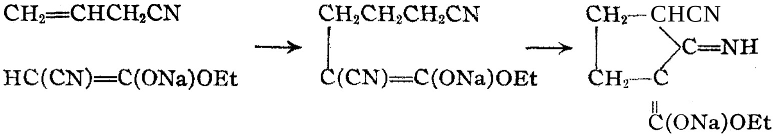
[22] Best and Thorpe, *J. Chem. Soc.*, *95, 685* (1909).

[23] Michael, Ber., **33, 3757** (1900).

[24] Hope, *J. Chem. Soc.*, 101,892 (1912); Ingold, Shoppee and Thorpe, *ibid.*, **1477** **(1926).**

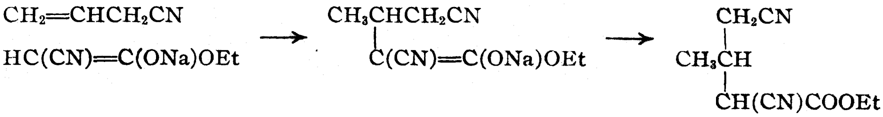
tion of reactions where this type of addition might be expected to be favored.

Allyl cyanide was chosen as a readily accessible β,γ-unsaturated compound of the same type as vinylacetic ester. If this added sodium enol cyanacetic ester in the above manner, then the ethyl compound of 2-imino-3-cyanocyclopentane-1-carboxylate (XLV) would be formed, a compound that has been described by Thorpe and Best.[22]



XLIV XLV

When this reaction was carried out in alcohol, or alcohol-free benzene, none of the cyclic imino compound could be detected. A very good yield of sodium derivative of β-methyl α-carbethoxyglutaronitrile (XLVI) was obtained



$$\begin{array}{l} CH_2{=}CHCH_2CN \\ HC(CN){=}C(ONa)OEt \end{array} \longrightarrow \begin{array}{l} CH_3CHCH_2CN \\ \quad| \\ C(CN){=}C(ONa)OEt \end{array} \longrightarrow \begin{array}{l} \quad CH_2CN \\ \quad\ | \\ CH_3CH \\ \quad\ | \\ \quad CH(CN)COOEt \end{array}$$

XLVI XLVII

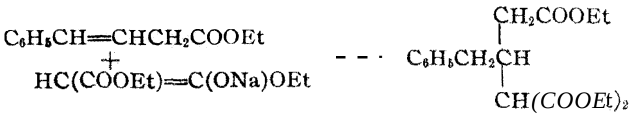
Similarly sodium enol a-cyanopropionic ester and allyl cyanide gave sodium enol α,β-dimethyl-γ-carbethoxyglutaronitrile (XLVIII) by migration of CH_3, although in this case a quantity of resinous material was also formed

$$\begin{array}{l} CH_2{=}CHCH_2CN \\ CH_3C(CN){=}C(ONa)OEt \end{array} \qquad \begin{array}{l} CH_3CHCN \\ \quad\ | \\ CH_3CH \\ \quad\ | \\ \quad C(CN)C(ONa)OEt \end{array}$$

XLVIII

The absence of β,γ-addition with allyl cyanide may be due to the great tendency of this nitrile to rearrange to the more stable α,β-unsaturated isomer. Since styrylacetic acid (β,γ-derivative) is known to be far more stable toward alkali than y-phenylcrotonic acid (α,β-isomer)[25] addition to styrylacetic ester was therefore examined. Vorlander and Strunck showed that sodium enol malonic ester adds to styrylacetic ester apparently through the α,β-derivative to give β-benzyl-γ-carbethoxyglutaric ester (XLIX). However, there is obviously no means of deciding from the structure of the addition product, at which carbon the hydrogen of the addendum had united

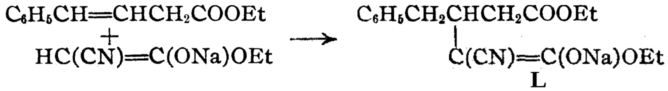
[25] Vorländer and Strunck, *Ann.*, 239, 345 **(1906).**



$$C_6H_5CH{=}CHCH_2COOEt + HC(COOEt){=}C(ONa)OEt \dashrightarrow C_6H_5CH_2\overset{CH_2COOEt}{\underset{CH(COOEt)_2}{CH}}$$

XLIX

We found that sodium enol cyanacetic ester similarly gave the sodium derivative of *β*-benzyl-*γ*-cyanoglutaric ester (L) and no cyclic imino compound was found in the reaction product.

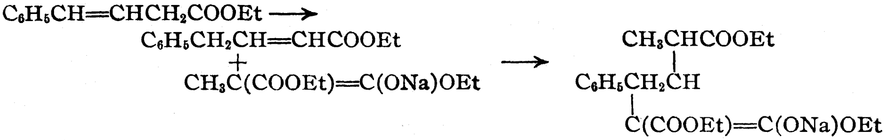


$$C_6H_5CH{=}CHCH_2COOEt + HC(CN){=}C(ONa)OEt \longrightarrow C_6H_5CH_2\underset{C(CN)=C(ONa)OEt}{CH}CH_2COOEt$$

L

Addition of sodium enol a-cyanopropionic ester to styrylacetic ester gave a cyano ester from which no identifiable acids could be obtained after hydrolysis with caustic alkali, nor was there any indication of the formation of an imino derivative.

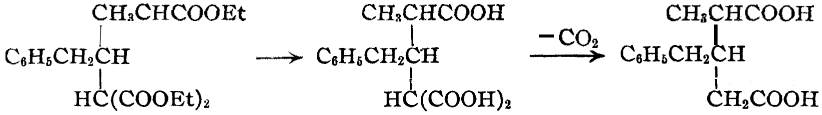
Addition of sodium enol methylmalonic ester to styrylacetic ester gave the sodium derivative of *α*-methyl-*β*-benzyl-*γ*-carbethoxyglutaric ester (LI), showing that migration of the methyl group had taken place as well as apparent addition to the a,@-isomer of styrylacetic ester.



$$C_6H_5CH{=}CHCH_2COOEt \longrightarrow C_6H_5CH_2CH{=}CHCOOEt + CH_3C(COOEt){=}C(ONa)OEt \longrightarrow C_6H_5CH_2\overset{CH_3CHCOOEt}{\underset{C(COOEt)=C(ONa)OEt}{CH}}$$

LI

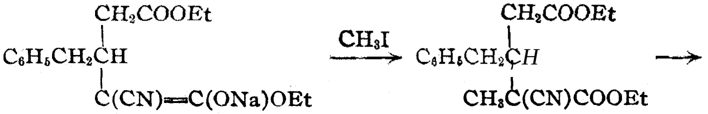
Upon saponification of the ester (LII), two stereomeric tricarboxylic acids were obtained, melting at 195 and 118'. These acids when heated above their melting points lost carbon dioxide and gave the isomeric *α*-methyl-*β*-benzylglutaric acids (LIV), melting at 139 and 97°, respectively.



$$C_6H_5CH_2\overset{CH_3CHCOOEt}{\underset{HC(COOEt)_2}{CH}} \longrightarrow C_6H_5CH_2\overset{CH_3CHCOOH}{\underset{HC(COOH)_2}{CH}} \xrightarrow{-CO_2} C_6H_5CH_2\overset{CH_3CHCOOH}{\underset{CH_2COOH}{CH}}$$

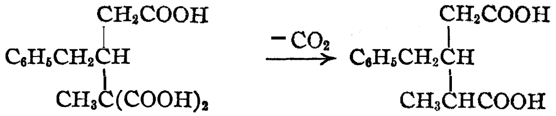
LII LIII Two forms LIV Two forms

By methylation of the sodium derivative of *β*-benzyl y-cyanoglutaric ester (L), *γ*-methyl-*β*-benzyl-*γ*-cyanoglutaric ester (LV) was obtained and this upon hydrolysis gave *γ*-methyl-*β*-benzyl-*γ*-carboxyglutaric acid (LVI), melting at 177°. This acid on heating above 177" gave *α*-methyl-*β*-benzylglutaric acid (LIV), m. p. 139°, which was identical with the acid of the same melting point obtained above.



$$C_6H_5CH_2\overset{CH_2COOEt}{\underset{C(CN)=C(ONa)OEt}{CH}} \xrightarrow{CH_3I} C_6H_5CH_2\overset{CH_2COOEt}{\underset{CH_3C(CN)COOEt}{CH}} \longrightarrow$$

L LV

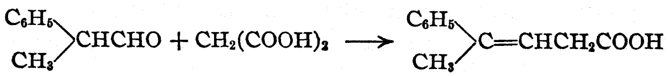


$$\begin{array}{c}CH_2COOH\\ |\\ C_6H_5CH_2CH\\ |\\ CH_3C(COOH)_2\end{array} \xrightarrow{-CO_2} \begin{array}{c}CH_2COOH\\ |\\ C_6H_5CH_2CH\\ |\\ CH_3CHCOOH\end{array}$$

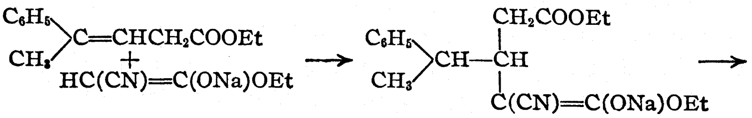
LVI LIV

Evidently to establish the constitution of the tricarboxylic acid, m. p. 118°, and of the dicarboxylic acid, m. p. 97°, derived from it, it was necessary to compare it with γ-methyl-γ-phenyl-β-aceticbutyric acid (LX).

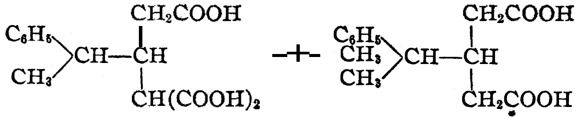
For this purpose hydratropic aldehyde was condensed with malonic acid in the presence of diethylamine, and the ester of the γ-methyl-γ-phenylbutenoic acid (LVII) so obtained was treated with sodium enol cyanacetic ester



LVII



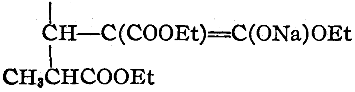
LVIII



LIX LX

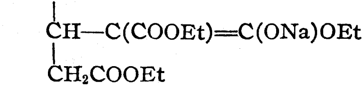
The cyano ester was hydrolyzed to the tricarboxylic acid (LIX) melting at 162°, which upon heating lost carbon dioxide and gave y-methyl-γ-phenyl-β-aceticbutyric acid, m. p. 88° (LX).

In the addition of sodium enol methylmalonic ester to styrylacetic ester, the methyl group evidently assumed the α-position and isomerization of the styrylacetic ester to y-phenylcrotonic ester occurred. This rearrangement may have anteceded the addition but it is more probable that it took place during the process and that it was associated with the maximal neutralization of the positive energy of the sodium. A comparison of the structures of the two possible addition products (LXI) and (LXII)



$$\begin{array}{l}CH_2C_6H_5\\ |\\ CH{-}C(COOEt){=}C(ONa)OEt\\ |\\ CH_3CHCOOEt\end{array}$$

LXI



$$\begin{array}{l}CH_3CHC_6H_5\\ |\\ CH{-}C(COOEt){=}C(ONa)OEt\\ |\\ CH_2COOEt\end{array}$$

LXII

shows that the negative radicals of (LXI) are more symmetrically arranged about the positive nucleus CH—C(COOEt)=C(ONa)OEt and that (LXI) should therefore be the intramolecularly better neutralized compound.

Experimental

A. Addition of Alkylmalonic Esters to Fumaric Ester

Propane-α,β,γ,γ-tetracarboxylic ester was prepared by the addition of malonic ester to fumaric ester in the presence of a small amount of sodium ethoxide;'' yield, 90% of theory, b. p. 187° (5 mm.).

Propane-α,β,γ,γ-tetracarboxylic acid was prepared from the above ester by saponification with 20% barium hydroxide solution and decomposing the sparingly soluble barium salt obtained with acid. The tetracarboxylic acid was extracted with ether and crystallized from the ether solution as a fine powder, m. p. 153°.

Anal. Calcd for $C_7H_8O_8$: C, 38.19; H, 3.64. Found: C. 38.36; H, 3.80.

Butane-α,β,γ,γ-tetracarboxylic ester was obtained by adding 22 g. of propane-α,β,γ,γ-tetracarboxylic ester to an ethereal suspension of anhydrous sodium ethoxide prepared from 1.8 g. of sodium, and methylating by addition of 10 g. of methyl iodide to the solution of sodium derivative, the mixture being cooled in ice. After standing for eight hours at room temperature, the product was worked up in the usual way; yield 21 g. of ester boiling at 180° (3 mm.).

Anal. Calcd. for $C_{16}H_{27}O_8$: C, 55.34; H, 7.78. Found: C, 55.50; H, 7.95.

Upon treatment of this ester with an ethereal suspension of sodium ethoxide, followed by methyl iodide, the main products were those of fission into fumaric and methylmalonic esters; 16 g. of ester was added to sodium ethoxide from 1.2 g. of sodium and after five minutes 8 g. of methyl iodide was added, the whole mixture standing at 0° for twelve hours. Upon working up there were obtained: 10 g. of ester, b. p. 95–120° (10 mm.), fumaric, dimethylmalonic esters; 4 g. of ester, b. p. 120–180° (3 mm.), unchanged ester.

Butane-α,β,γ,γ-tetracarboxylic acid was obtained by saponifying the ester with 20% caustic potash or barium hydroxide solution. The acid was liberated with hydrochloric acid and extracted with ether. It crystallized in transparent nodules from ether or acetone and ligroin and melted at 170°.

Anal. Calcd. for $C_8H_{10}O_8$: C, 41.03; H, 4.27. Found: C, 40.82; H, 4.46.

Butane-β,γ,δ,δ-tetracarboxylic ester is formed when fumaric ester is added to methylmalonic ester in the presence of an equivalent of sodium ethoxide in ethereal solution. This ester was previously obtained by Auwers, Kobner and Meyenberg,[27] and Michael[a] but described as butane-α,β,γ,γ-tetracarboxylic ester. Michael showed that this ester formed a sodium derivative, which readily reacted with methyl iodide and gave a quantitative yield of pentane-β,γ,δ,δ-tetracarboxylic ester and which, upon hydrolysis, gave α,γ-dimethyltricarballylic acid.

Butane-β,γ,δ,δ-tetracarboxylic acid was prepared by saponifying the ester with caustic potash. It was extracted with ether and crystallized from an ether-ligroin mixture in large nodules. There was no change in melting point upon fractional crystallization, so it was concluded that this acid, melting at 176°, was probably a pure stereomeric form. Hope[29] obtained an acid, melting at 155°, which he considered to be a mixture of two stereomeric forms, from the ester obtained in the addition of sodium enol malonic ester to citraconic ester.

Anal. Calcd. for $C_8H_{10}O_8$: C, 41.03; H, 4.27. Found: C, 41.21; H, 4.42.

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[26] Ruhemann and Cunnington, J. *Chem. Soc.*, 73, 1007 (1898).

[27] Auwers. Kobner and Meyenberg, *Ber.*, 24, 2890 (1891).

[28] Michael, *ibid.*, 33, 3761 (1900).

[29] Hope, J. *Chem. Soc.*, 101, 901 (1912).

Pentane-β,γ,δ,δ-tetracarboxylic acid was prepared by saponification of the ester obtained upon treating the above **butane-β,γ,δ,δ-tetracarboxylic** ester with sodium ethoxide and methyl iodide at 0°. Recrystallized from acetone–ligroin mixture, m. p. 166°.

Anal. Calcd. for $C_9H_{12}O_8$: C, 43.54; H, 4.84. Found: C, 43.28; H, 4.90.

Pentane-α,β,γ,γ-tetracarboxylic Ester.—Prepared by treating sodium enol propane-α,β,γ,γ-tetracarboxylic ester with ethyl iodide, in ethereal solution, in the cold. The ester boiled at 180° (3 mm.).

Anal. Calcd. for $C_{17}H_{29}O_8$: C, 56.51; H, 8.03. Found: C, 56.65; H, 8.00.

Nine grams of ester was added to sodium ethoxide from 0.7 g. of sodium and after five minutes 8 g. of methyl iodide was added, the whole mixture standing on ice for twelve hours. Upon working up, there was obtained 8 g of ester, b. p. 180° (3 mm.), which proved to be unchanged ester, since upon saponification it gave pentane-α,β,γ,γ-tetracarboxylic acid, m. p. 177°.

Pentane-α,β,γ,γ-tetracarboxylic acid was obtained by saponifying the ester with caustic potash. It crystallized from ether in nodules, m. p. 177".

Anal. Calcd. for $C_9H_{12}O_8$: C, 43.54; H, 4.84. Found: C, 43.35; H, 4.77.

Pentane-α,α,β,γ-tetracarboxylic ester was obtained when fumaric ester was added to sodium enol ethylmalonic ester, formed by adding ethylmalonic ester to an equivalent of anhydrous sodium ethoxide suspended in ether. This ester, previously described as pentane-α,β,γ,γ-tetracarboxylic ester, was obtained by Michael,[28] who also showed that it formed a sodium derivative which, upon methylation, gave a quantitative yield of hexane-β,β,γ,δ-tetracarboxylic ester.

Pentane-α,α,β,γ-tetracarboxylic acid was prepared by saponifying the ester with caustic potash. It crystallized from ether or acetone–ligroin in transparent nodules, melting at 179° with decomposition, and, since no separation was obtained upon fractional crystallization, it was concluded that this acid represented a single stereomeric form.

Anal. Calcd. for $C_9H_{12}O_8$: C, 43.54; H, 4.84. Found: C, 43.75; H, 5.05.

Hexane-β,β,γ,δ-tetracarboxylic acid was prepared by saponifying the ester obtained by treating pentane-α,α,β,γ-tetracarboxylic ester with sodium ethoxide and methyl iodide in ether solution at 0°. Recrystallized from acetone–ligroin mixture, m. p. 170°.

Anal. Calcd. for $C_{10}H_{14}O_8$: C. 45.80; H, 5.34. Found: C, 45.72; H, 5.51.

B. Addition of Alkylcyanacetic Esters to Crotonic Ester

Addition of a-Cyanopropionic Ester to Crotonic Ester.—a-Cyanopropionic ester was prepared by methylation of sodium enol cyanacetic ester and freed from unchanged cyanacetic ester by shaking with successive small quantities of 5% caustic potash.

To a solution of 4.7 g. of sodium dissolved in 70 cc. of absolute alcohol, 25.5 g. of a-cyanopropionic ester was added, followed by 23 g. of crotonic ester. The mixture was heated on the water-bath for twenty-four hours. The cooled product was then poured into 500 cc. of ice water containing 13 g. of acetic acid and extracted with ether. The ethereal extract was washed with 10% sodium carbonate, followed by distilled water, the neutral esters dried and fractionated. Some low-boiling material came over first and then two main fractions were collected: 24 g., representing a 50% yield of **γ-cyano-α,β-dimethylglutaric** ester, distilled at 145–148° (3 mm.). This was a colorless liquid, which gave no coloration with alcoholic ferric chloride.

Anal. Calcd. for $C_{12}H_{19}O_4N$: C, 59.75; H, 7.88. Found: C, 59.65; H, 7.95.

Eleven grams of ester, collected between 160 and 185" (3 mm.), gave a deep red coloration with alcoholic ferric chloride. After redistillation, a fraction boiling at 182° (3 mm.) was obtained which was analyzed

And, Calcd. for $C_{12}H_{19}O_4N$: C, 59.75; H, 7.88; N, 5.82. Found: C, 59.47; H, 7.6; N, 5.7.

Upon hydrolyzing 3 g. of this high-boiling ester with hydrochloric acid (1:1), a small quantity of a ketonic compound, b. p. 50–120° (10 mm.), was obtained together with a sirupy acid. The ketonic compound with semicarbazide acetate gave a crystalline semicarbazone within one hour. This was recrystallized from dilute aqueous alcohol and melted at 224".

Anal. Calcd. for $C_7H_{13}ON_3$: C, 54.2; H, 8.38; N, 27.1. Found: C, 54.79; H, 7.34; N, 19.0.

These figures do not correspond with any simple derivative of cyclopentanone.

α,β-Dimethyl-γ-cyanoglutaric acid was obtained by saponification of or,@-dimethyl-γ-cyanoglutaric ester, b. p. 145–148° (3 mm.), with 20% caustic potash containing a small amount of alcohol. Immediately upon warming, the ester dissolved. After acidifying the well-cooled solution, the cyano acid was extracted with ether. It was a sirup which resisted all attempts to make it crystallize

Anal. Calcd. for $C_8H_{11}O_4N$: C, 51.89; H, 5.95. Found: C, 51.56; H, 6.03.

When boiled for one hour with concentrated hydrochloric acid, the above α,β-dimethyl-γ-cyanoglutaric acid gave a small amount of α,β-dimethylglutarimide, m. p. 112°, together with a sirupy cyano acid from which, on treatment with alkali, a liquid α,β-dimethylglutaric acid was prepared. This was characterized as a *trans* derivative by conversion into a,@-dimethylglutaricdianilide The α,β-dimethylglutaric acid was mixed with an excess of aniline and heated at 180° for one hour. The neutral dianilide thus formed crystallized in fine needles from mixture of ether and ligroin and melted at 216°.

Anal. Calcd. for $C_{19}H_{22}O_2N_2$: C, 73.53; H, 7.1. Found: C, 73.27; H, 7.31.

The above α,β-dimethylglutaric dianilide was identical with the dianilide prepared from an authentic sample of the ***trans*** α,β-dimethylglutaric acid.

α,β-Dimethyl-γ-carboxyglutaric acid was prepared by complete hydrolysis of the ester boiling at 147° (3 mm.), or of the above cyano acid by boiling it with 20% caustic potash for eight hours when ammonia ceased to be evolved. The acid solidified on standing and was recrystallized from an ether–ligroin mixture as fine prisms, m. p. 142°.

Anal. Calcd. for $C_8H_{12}O_6$: C, 47.07; H, 5.88. Found: C, 46.95; H, 6.00.

This acid was shown by mixed melting point to ***be not*** identical with the α,β-dimethyl-γ-carboxyglutaric acid, m. p 145°, obtained by condensation of the enolic sodium derivative of malonic or cyanacetic esters with tiglic ester. From the ease of hydrolysis of the parent ester, and the general properties of the acid, it is probable that it is a stereomer of α,β-dimethyl-γ-carboxyglutaric acid.

α,β-Dimethyl-γ-cyanoglutaric acid was obtained as an uncrystallizable sirup by saponifying the addition product of sodium enol cyanacetic ester to tiglic ester.[30]

Anal. Calcd. for $C_8H_{11}O_4N$: C, 51.89; H, 5.95. Found: C, 51.63; H, 6.10.

Upon boiling with concentrated hydrochloric acid, it gave some α,β-dimethylglutarimide, m. p. 113°, together with a cyano acid. Alkali hydrolysis of this acid, however, gave ***trans*** α,β-dimethylglutaric acid, characterized by the dianilide, m. p. 216'.

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[30] Michael and Ross. Ref. 6. p. 4007.

β,γ-Dimethyl-γ-cyanoglutaric acid was prepared, for comparison with the above cyanoglutaric acids, by the action of methyl iodide upon the sodium derivative of β-methyl-γ-cyanoglutaric ester. It readily crystallized in large prisms, m. p. 152°, and upon boiling with hydrochloric acid gave about equal quantities of α,β-dimethylglutarimide and the trans cyano acid. Thorpe and Young[31] synthesized this acid by the same method, but gave the melting point as 132–133°.

Anal. Calcd. for $C_8H_{11}O_4N$: C, 51.89; H, 6.95. Found: C, 51.78; H, 5.96.

Attempted Addition of Sodium Enol Ethylmalonic Ester to Crotonic Ester.—a-Carboxybutyric ester was obtained by treating sodium enol malonic ester with ethyl iodide, and the product was purified from malonic ester by shaking four times with a third of its volume of 25% caustic potash.

Four and eight-tenths grams of sodium was pulverized and dissolved in 9.5 g. of absolute alcohol in ether solution. To the anhydrous sodium ethoxide, 38 g. of α-carboxybutyric ester was added, followed by 23 g. of crotonic ester and the mixture heated on the water-bath for six hours. The ice-cooled mixture was then washed with water containing a little more than an equivalent quantity of acetic acid. The ether solution was extracted with 10% sodium carbonate, followed by distilled water, dried and the neutral esters distilled; 35 g. of ester boiled up to 150° (25 mm.), consisting mainly of unchanged a-carboxybutyric ester and with some crotonic ester; 7 g. distilled from 140–152° (4 mm.), which consisted of a-ethylidene β-methylglutaric ester (or so-called dicrotonic ester). This was proved by analysis of the acid, m. p. 129°, obtained upon saponification of this ester.[32]

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.82; H, 7.56. Found: C, 56.04; H, 7.3.

There was also obtained 4 g. of ester boiling at 152–159° (4 mm.), which upon saponification gave a sirupy, uncrystallizable acid. The small yield of this material did not permit further examination, although it probably represented the addition product of ethylmalonic to crotonic ester.

Addition of Sodium Enol a-Cyanobutyric Ester to Crotonic Ester.—a-Cyanobutyric ester was prepared from sodium enol cyanacetic ester and ethyl iodide. The product was shaken with successively small amounts of 5% caustic potash in order to remove unchanged cyanacetic ester.

A solution of 4.7 g. of sodium in 70 cc. of absolute alcohol was mixed with 28 g. of α-cyanobutyric ester and then with 23 g. of crotonic ester, and the mixture heated on the water-bath for twenty-four hours. The cooled product was poured into 500 cc. of water containing 13 g. of acetic acid and the solution extracted with ether. The ethereal extract was washed with 10% sodium carbonate, then with distilled water, dried and the neutral esters distilled. About 25 g. distilled up to 140° (15 mm.), which consisted of unchanged esters. The 17 g. that passed over at 153° (3 mm.) proved to be γ-cyano-a-ethyl-P-methylglutaric ester, representing a 33% yield. It was a colorless liquid which gave no color with alcoholic ferric chloride.

Anal. Calcd. for $C_{13}H_{21}O_4N$: C, 61.18; H, 8.23. Found: C, 60.95; H, 8.30.

There was also obtained a fraction of ester, boiling at 160–165° (3 mm.), which gave a deep red coloration with alcoholic ferric chloride. This higher-boiling ester was probably homologous with the similar ester formed in the addition of sodium enol a-cyanopropionic ester to crotonic ester.

Anal. Calcd. for $C_{13}H_{12}O_4N$: C, 61.18; H, 8.23. Found: C, 60.56; H, 8.01.

γ-Cyano-α-ethyl-β-methylglutaric acid was obtained by saponification of the ester,

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[31] Thorpe and Young, J. Chem. Soc., 83, 357 (1903).

[32] V. Pechmann, Ber., 33, 3340 (1900); and Michael, *ibid.*, 33, 3760 (1900).

b. p. 153' (3 mm.), with alcoholic potash, the mixture being gently boiled until the ester had dissolved. Upon acidifying, the acid was extracted with ether and crystallized in prisms from a mixture of ether and ligroin, m. p. 147". This cyano acid accounted for 60% of the product of saponification; only a residual sirup remained.

Anal. Calcd. for $C_9H_{13}O_4N$: C, 54.26; H, 6.53. Found: C, 54.15; H, 6.7.

α-Ethyl-β-methylglutarimides.—Boiling the above cyano acid with hydrochloric acid (1:1) gave a mixture of two isomeric imides. The tnain product melted at 92° and crystallized in fine needles from an ether–ligroin mixture.

Anal. Calcd. for $C_8H_{13}O_2N$: C, 61.94; H, 8.38. Found: C, 62.16; H, 8.6.

From the mother liquor the second imide melting at 102°, which crystallized in large prisms, was obtained. By boiling the above-mentioned sirupy cyano acid, more of this imide, m. p. 102°, was obtained. This was apparently formed from a stereomeric *cis* form of the a-ethyl-p-methyl-y-cyanoglutaric acid, which may occur in four racemic forms.

Anal. Found: C, 62.05; H, 8.5.

Cis **α-Ethyl-β-methylglutaric** acid was obtained by hydrolysis of the above imide, m. p. 92°, by boiling with hydrochloric acid for six hours. It crystallized in prisms from a mixture of chloroform and ligroin and melted at 88°.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.18; H, 8.04. Found: C, 55.13; H, 8.16.

α-Ethyl-β-methyl-γ-carboxyglutaric acid was obtained by complete hydrolysis of the ester, b. p. 153° (3 mm.), or of the cyano acid, m. p. 147°, with caustic potash. It crystallized in fine prisms, melting at 143°.

Anal. Calcd. for $C_9H_{14}O_6$: C, 49.53; H, 6.42. Found: C, 49.56; H, 6.53.

Addition of Sodium Enol Cyanacetic Ester to a-Ethyl Crotonic Ester.—To a solution of 2.3 g. in 35 cc. of absolute alcohol, 11.3 g. of cyanacetic ester was added, followed by 14.2 g. of α-ethylcrotonic ester (b. p. 160"). The mixture was heated on the water-bath for twenty-four hours and the material worked up as usual; yield, 60% of addition product.

α-Ethyl-β-methyl-γ-cyanoglutaric ester distilled at 154° (4 mm.).

Anal. Calcd. for $C_{13}H_{21}O_4N$: C, 61.18; H, 8.23. Found: C, 61.06; H, 8.40,

α-Ethyl-β-methyl-γ-cyanoglutaric acid was prepared by saponifying the above ester with alcoholic potash. It crystallized in large prisms, melting at 132".

And. Calcd. for $C_8H_{13}O_4N$: C, 54.26, H, 6.23. Found: C, 54.22; H, 6.08.

Upon boiling the cyano acid with hydrochloric acid, a small amount (5%) of a mixture of the α-ethyl-β-methylglutarimides was obtained, but the main product was a sirupy cyano acid that could not be crystallized. This was apparently or-ethyl-@-methyl-y-cyanobutyric acid, since, upon complete hydrolysis, it gave *trans* or-ethyl-& methylglutaric acid, m. p. 101°. This acid crystallized in large prisms from a mixture of chloroform and ligroin. It had previously been prepared by v. Pechmann,[32] from α-ethylidene-β-methylglutaric acid, who only described one form, which from the above synthesis is apparently the *trans* stereomer.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.18; H, 8.06. Found: C, 55.25; H, 8.18.

a-Ethyl-@-methyl-γ-carboxyglutaric acid was obtained by complete hydrolysis of the ester, b. p. 154° (4 mm.), or of the cyano acid, m. p. 132°, with caustic potash. It crystallized in needles, m. p. 141°.

And. Calcd. for $C_9H_{14}O_6$: C, 49.53; H, 6.42. Found: C, 49.82; H, 6.69.

Ethylation of γ-Cyano-β-methylglutaric Ester.—γ-Cyano-β-methylglutaric ester was prepared by the addition of crotonic ester to sodium enol cyanacetic ester in alcoholic solution. The ester distilled as a colorless liquid, b. p. 147° (3 mm.).[33] To a suspension of sodium ethoxide prepared by the action of **4.8** g. of absolute alcohol upon **2.5** g. of pulverized sodium, **23** g. of γ-**cyano**-β-**methylglutaric** ester was added. After standing until the formation of the soluble sodium derivative was completed, **17** g. of ethyl iodide was added and the mixture stood for two hours at room temperature. After warming on the steam-bath for half an hour, the product was worked up in the usual way. γ-**Ethyl**-β-**methyl**-γ-**cyanoglutaric** ester boiled at 152° (**4** mm.).

Anal. Calcd. for $C_{13}H_{21}O_4N$: C, **61.18**; H, **8.23**. Found: C, **61.29**; H, **8.42**.

γ-Ethyl-β-methyl-γ-cyanoglutaric acid was obtained through saponification with alcoholic potash. It crystallized from ether–ligroin mixture in long prisms, m. p. 139°. The amount of this cyano acid accounted for 80% of the product of saponification.

Anal. **Calcd.** for $C_9H_{13}O_4N$: C, 5426; H, **6.53**. Found: C, **54.11**; H, **6.63**.

Upon boiling γ-ethyl-β-methyl-γ-cyanoglutaric acid with dilute hydrochloric acid for one hour, there was formed a small amount of the two α-ethyl-β-methylglutarimides (less than 5%), but the main product was a sirupy cyano acid which could not be crystallized. It was apparently α-ethyl-β-methyl-γ-cyanobutyric acid, since, upon complete hydrolysis, it gave *trans* **α-ethyl-β-methylglutaric** acid, m. p. **101°**.

γ-Ethyl-β-methyl-γ-carboxyglutaric acid.—Upon boiling γ-**ethyl**-β-**methyl**-γ-**cyanoglutaric** ester, or the corresponding cyano acid, with 30% caustic potash for twenty-four hours, a sirupy tricarboxylic acid was obtained which could not be crystallized.

Anal. Calcd. for $C_9H_{14}O_6$: C, **49.53**; H, **6.42**. Found C, **49.28**; H, **6.62**.

When boiled with hydrochloric acid, the **tricarboxylic** acid lost carbon dioxide to form a mixture of *cis* and *trans* a-ethyl-j3-methylglutaric acids.

C. Addition to β,γ-Unsaturated Compounds

Addition of **Sodium Enol** Cyanacetic Ester to **Allyl** Cyanide.—Ally1 cyanide was prepared from cuprous cyanide by the method described in "Organic Syntheses" (Vol. VIII, p. 4); **5.7** g. of sodium was dissolved in **85** cc. of absolute alcohol and 28 g. of **cyanacetic** ester added. After cooling, **17** g. of **allyl** cyanide was added and, as there was a noticeable evolution of heat as the solid derivative dissolved, the flask was placed in ice water The mixture was gently **refluxed** upon the water-bath for sixteen hours. The product was cooled, mixed with dilute acetic acid and extracted with ether; **40** g. of **β-methyl-γ-carbethoxyglutaronitrile,** b. p. 160° (**3** mm.), was obtained, being a yield of 90%.

Anal. Calcd. for $C_9H_{12}O_2N_2$: C, 59.99; H, **6.66**. Found: C, **59.75**; H, **6.80**.

When the addition was **carried** out in xylene using alcohol-free sodium **enol cyanacetic** ester, prepared by precipitation from ether solution, the product was the same.

In each case the constitution of the cyano ester was proved by hydrolysis with 20% caustic potash, when β-methyl-γ-carboxyglutaric acid was obtained, m. p. 139° (Ref. **6,** p **4604).**

Addition of Sodium **Enol α-Cyanopropionic** Ester to **Allyl** Cyanide.——Thirty-two grams of a-cyanopropionic ester was added to a solution of 5.7 g. of sodium in absolute alcohol and then 17 g. of **allyl** cyanide, **carrying** out the operation as above. The neutral products, **12 g.,** distilling up to **110°** (**15** mm.), consisted apparently of unchanged material; 17 g. distilled at 152° (3 mm.) which was **α,β-dimethyl-γ-carbethoxyglutaronitrile,** and a resinous residue weighing **12** g. remained in the flask.

Anal. Calcd. for $C_{10}H_{14}O_2N_2$: C, **61.85**; **H, 7.22**. Found: C, **61.72**; H, **7.36**.

Upon hydrolysis with **20%** caustic potash, the cyano ester gave a,@-dimethyl-7-

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[33] Darbishire and Thorpe, J. *Chem. Soc.*, **87, 1716 (1905).**

carboxyglutaric acid, m. p. 142". This was identified by analysis, direct comparison and a mixed melting point with a sample of the acid, prepared by addition of sodium enol α-cyanopropionic ester to crotonic ester.

Addition of Sodium Enol Cyanacetic Ester to Styrylacetic Ester.—To a solution of **1.2 g.** of sodium in 20 cc. of absolute alcohol, was added **5.8** g. of cyanacetic ester, followed by **9.5** g. of styrylacetic ester, and the mixture heated for sixteen hours on the water-bath. After working up in the usual way, a yield of **10** g. of addition product, boiling at **193°** (3 mm.), was obtained. The formation of enolic compounds could not be detected.

Anal. Calcd. for $C_{17}H_{21}O_4N$: C, **67.33;** H, **6.93.** Found: C, **67.15; H, 7.10.**

β-Benzyl-γ-carboxyglutaric acid was obtained through treatment of the above ester with caustic potash. It crystallized in large transparent prisms, melting at 158° with decomposition. This acid should be identical with the acid obtained by Vorlander and Strunck[34] through the addition of sodium enol malonic ester to styrylacetic ester, although their acid melted at **146°**.

Anal. Calcd. for $C_{13}H_{14}O_6$: C, **58.64;** H, **5.26** Found: C, **58 41;** H, **5.35.**

The above acid gave β-benzylglutaric acid on heating to 165° for thirty minutes. It crystallized in large prisms from an ether–ligroin solution and, like Vorländer and Strunck's acid, melted at **102°**

γ-Methyl-β-benzyl-γ-cyanoglutaric ester was obtained by treatment of the sodium derivative of the above ester in ether solution with methyl iodide. It boiled at 194° (3 mm.).

Anal. Calcd. for $C_{18}H_{23}O_4N$: C, **68.14,** H, **7.25.** Found: C, **68.22;** H, **7.41.**

γ-Methyl-β-benzyl-γ-carboxyglutaric acid was prepared through hydrolysis of the above cyano ester with caustic potash. It crystallized in large prisms from acetone–ligroin mixture and melted at 177° with decomposition.

Anal. Calcd. for $C_{14}H_{16}O_6$: C, **59.99;** H, **5.71.** Found: C, **60.18;** H, **5.93.**

α-Methyl-β-benzylglutaric acid.—This acid was heated at **180°** for thirty minutes and the decomposition product crystallized from a mixture of ether and ligroin. Only one acid was isolated and this melted at 139° after recrystallization.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, **66.1;** H, **6.78.** Found: C, **66.23;** H, **6.90.**

Addition of Sodium Enol Methylmalonic Ester to Styrylacetic Ester.—To a suspension of anhydrous sodium ethoxide prepared from **2.3** g. of sodium, **17.5** g. of methylmalonic ester was added, followed by **19** g. of styrylacetic ester and the mixture was heated upon the water-bath for six hours. After working up as usual, **15** g. of unchanged esters, b. p. up to 120° **(10** mm.) was obtained and **15** g. of the addition product ester, boiling at 197° **(3** mm.) There was also a small amount of high-boiling ester which distilled at 222° (3 mm.).

Anal. Calcd. for $C_{19}H_{26}O_6$: C, **65.13;** H, **7.43.** Found: C, **65.28; H, 7.61.**

α-Methyl-β-benzyl-γ-carboxyglutaric acid.—The ester, boiling at 197° (3 mm.), was saponified with caustic potash. After acidifying, the tricarboxylic acids were extracted with ether. Upon addition of ligroin, an acid crystallized out which melted at **197"** upon purification.

Anal. Calcd. for $C_{14}H_{16}O_6$: C, **59.99;** H, **5.71.** Found: C, **59.71;** H, **6.00.**

A second isomeric α-methyl-β-benzyl-γ-carboxyglutaric acid was obtained from the mother liquor left after crystallizing out the form of m. p 197°. It was recrystallized from chloroform and melted at 118°.

A d . Found: C, **59.81;** H, **5.9.**

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[34] Vorländer and Strunck, Ann., **345,239 (1906).**

α-Methyl-β-benzylglutaric Acid.—When the a-methyl-p-benzyl-y-carboxyglutaric acid, melting at 195°, was decomposed by heating at 200° for twenty minutes, a mixture of the two forms of a-methyl-p-benzylglutaric acid was obtained. These were separated by crystallization from chloroform–ligroin mixture. The main product was the stereomer, m. p. 139°, identical with the acid obtained above from **γ-methyl-β-benzyl-γ-carboxyglutaric** acid. The other isomer present in small amount melted at 97°.

When α-methyl-β-benzyl-γ-carboxyglutaric acid, m. p. 118°, was heated at 150° for thirty minutes, the product consisted entirely of α-methyl-β-benzylglutaric acid, m. p. 97°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, **66.10;** H, **6.78.** Found: C, **66.18;** H, **6.95.**

Synthesis of **γ-Methyl-γ-phenyl-β-aceticbutyric** Acid.—Hydratropic aldehyde, prepared by Claisen's method[35] was condensed with malonic acid, by boiling a mixture of the aldehyde and malonic acid in alcoholic solution for six hours in the presence of a few drops of diethylamine. The product was poured into water, and extracted with ether. The acid was extracted from the ether solution by washing with sodium carbonate solution. Upon acidifying with hydrochloric acid an oil was obtained which was taken up in ether. The acid thus obtained was esterified by boiling with absolute alcohol containing a little sulfuric acid. The ester obtained was fractionally distilled and gave two main fractions; γ-methyl-γ-phenylbutenoic ester boiled at 156° **(10 mm.).**

Anal. Calcd. for $C_{13}H_{16}O_2$: C, **76.47;** H, 7.84. Found: C, **76.24;** H, **8.06.**

A smaller amount of the higher-boiling fraction of ester, 175–182° **(10** mm.), was apparently γ-methyl-γ-phenyl-α-carbethoxybutenoic ester.

A d . Calcd. for $C_{16}H_{20}O_4$: C, **69.56;** H, 7.25. Found: C, **69.32;** H, **7.40.**

y-Methyl-y-phenylbutenoic acid was obtained by saponification of the above ester, b. p. 156° **(10 mm.)**; it remained a sirup. Mayer and Stamm[36] previously obtained this acid, m. p. 75–78°, through the action of methylmagnesium iodide upon benzoylpropionic ester.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, **75.00;** H, **6.82.** Found: C, **74.73;** H, **7.06.**

y-Methyl-y-phenyl-a-carboxybutenoic Acid.—Upon saponification of the ester. b. p. 175–182° **(10** mm.), an acid was obtained melting at **151**"with evolution of gas.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, **65.46;** H, **5.45.** Found: C, **65.23;** H, **5.60.**

Addition of Sodium **Enol** Cyanacetic Ester to **γ-Methyl-γ-phenylbutenoic** Ester.—To a solution of **1.2** g. of sodium in 20 cc. of alcohol was added **5.7** g. of cyanacetic ester, followed by **10** g. of **γ-methyl-γ-phenylbutenoic** ester, and the mixture heated for twelve hours upon the water-bath. The product was worked up in the usual manner and 9 g. of ester, b. p. **198'** **(3** mm.), was obtained. This was the addition product, **γ-methyl-**γ-phenyl-α-cyano-β-aceticbutyric ester.

Anal. Calcd. for $C_{18}H_{23}O_4N$: C, **68.14;** H, **7.25.** Found: **C, 68.26;** H, **7.38.**

γ-Methyl-γ-phenyl-α-carboxy-β-aceticbutyric acid was obtained through saponifying the above ester with caustic potash. The acid crystallized in large prisms from an acetone–ligroin mixture which melted at **162'** with decomposition.

Anal. Calcd. for $C_{14}H_{16}O_6$: C, **59.99;** H, **5.71.** Found: C, **60.18;** H. **5.64.**

γ-Methyl-γ-phenyl-β-aceticbutyric acid was prepared by heating the above tricarboxylic acid to 165° for thirty minutes. The acid crystallized from a mixture of ligroin and ether in fine needles melting at 88°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, **66.10;** H, **6.78.** Found: **C, 66.11;** H, **6.63.**

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[35] Claisen, *Ber.*, 38, 702 (1905).

[36] Mayer and Stamm, *ibid.*, 56, **1424 (1923).**

Summary

1. The course of addition of a derivative of the sodium enol malonic ester type to an α,β-unsaturated ester proceeds according to the law of chemical neutralization. That addition product is therefore formed in which the positive energy of the sodium atom is best neutralized, since the maximal energy degradation is thus realized.

2. It has been shown that in the addition of sodium enol alkyl malonic esters to fumaric ester, the alkyl group migrates so that the addendum parts are alkyl and —C(COOEt)=C(ONa)OEt.

3. In the addition of sodium enol alkyl cyanacetic esters to crotonic ester, the addendum parts are similarly alkyl and —C(CN)=C(ONa)OEt.

4. In the addition to crotonic ester, the yield of addition product was greater in the case of sodium enol methylcyanacetic ester *(50%)* than with sodium enol ethylcyanacetic ester **(33%).** However, the yield of addition product is determined by several complex factors so that it is not possible from these experiments to make any statement regarding the relative ease of migration of the methyl and ethyl groups in these addition reactions.

5. In these reactions, the maximal chemical neutralization of the sodium is realized by the sodium remaining attached to the carbonyl oxygen atom in the malonic or cyanacetic groups. The sodium atom, however, becomes better neutralized than it was in the addendum by the spatial negative influence of the acquired carbethoxyl group.

6. Esters of the type $CHX(COOEt)—CHY—CZ(COOEt)_2$ [where X = R or H, Y = R, H or COOEt and Z = R or H, also R is an alkyl or aryl radical], apparently form enolic sodium derivatives containing the group —CH=C(ONa)OEt, but these immediately decompose to form ethylenic α,β-esters and sodium alkylmalonic esters. The retrogression of the free ester (A) by sodium is probably due to the formation of such an enolic sodium derivative, It would follow from this relationship that the sodium atom involved in the addition reactions specified under 2 and **3** above cannot migrate during the addition process. However, if the single carbethoxyl group of (A) can form an enolate, an amount of sodium corresponding to the relative acidity of the two enolic forms of ester (A) (Z = H), would migrate to the single carbethoxyl group according to the partition principle,[37] and spontaneous retrogression would lead to the re-formation of a further quantity of this sodium enol derivative. Thus, by this process, in agreement with the partition principle, an apparent balanced state would be achieved between the two possible stable sodium derivatives.

7. It has not been found possible to obtain addition to the γ-carbon atom of a β,γ-unsaturated ethylenic ester or nitrile. Addition occurs

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[37] Michael, *J. prakt. Chem.*, 60, 6 (1899).

in the case of allyl cyanide and styrylacetic ester at the α- and β-carbon atoms, with migration of an α-hydrogen atom.

CAMBRIDGE, MASSACHUSETTS

NOTES

Some New *p*-Bromophenacyl Esters.—In using the method of Reid and Judefind [THIS JOURNAL, 42, 1043 (1920)] for the identification of organic acids, we have prepared the following *p*-bromophenacyl esters which are not listed by these authors: trimethylacetate, m. p. 76.5°; isocaproate, m. p. 77.3°; enanthate, m. p. 69.2°; isoheptylate, m. p. 75.5°; pelargonate, m. p. 63.5°.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

S. G. POWELL

RECEIVED JANUARY 19, 1931
PUBLISHED MARCH 6, 1831

Preparation of N-o-Chlorobenzoyl-o-chlorobenzenesulfonamide.—Several years ago an investigation was undertaken in this Laboratory having for its object the preparation of diphenic sulfinide ("Diphensaccharin"). It was hoped that this compound might be sweet, or at least that its preparation would throw some light on the general problem of sweet taste *vs.* molecular structure. The method attempted was the internal condensation of chlorobenzoylchlorobenzenesulfonamide by loss of two atoms of chlorine from the molecule.

Preparation of N-o-Chlorobenzoyl-o-chlorobenzenesulfonamide, $ClC_6H_4CONHSO_2C_6H_4Cl$.—Ten grams of o-chlorobenzenesulfonamide was treated with 9.5 g. of o-chlorobenzoyl chloride and the mixture heated (180–190°) in an oil-bath for one hour. The dark brown mass was dissolved in acetone, the solution filtered, and the solid again precipitated by the use of petroleum ether. The solid was heated on a clay plate (70–80°) until it was perfectly dry and odorless. Repeated crystallizations from dilute ethanol or dilute acetic acid finally gave a product with a constant melting point of 154–155°; white platelets, having a faint bitter taste, yield about 11 g.

Anal. Calcd. for $C_{13}H_9O_3Cl_2NS$: C, 47.27; H, 2.72; N, 4.24; Cl, 21.52; S, 9.70. Found: C, 47.24; H, 2.60; N, 4.19; Cl, 21.40; S, 9.76.

In attempting to prepare diphenic sulfinide from the compound named above, it was heated alone and in different solvents, and treated with metals and other reagents under a variety of conditions. Seventy-two experiments were carried out, only two of which gave any indication of success. In these cases the material was heated in amyl alcohol solution with copper powder and sodium iodide.[1] A compound was secured having a melting point of 255–258°. It was contaminated with amyl alcohol, which was removed in part by application of heat. The yield was small and complete purification was not possible. Analysis for sulfur gave 8.67%, while theory calls for 12.35%. The compound had a bitter taste. Repetitions of this experiment did not again yield this compound, and lack of starting materials forced the abandonment of the project. In view of the known instances in which seven- and eight-membered ring compounds have been made from diphenic acid, the failure of this synthesis is without explanation, and seems worthy of report.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
THE UNIVERSITY OF ARKANSAS
FAYETTEVILLE, ARKANSAS
E. WERTHEIM

RECEIVED DECEMBER 2, 1930
PUBLISHED MARCH 6, 1931

The p-Bromoanilides of Isobutyric and Isovaleric Acids.—For purposes of comparison in identification work in this Laboratory it was desired to have samples of the *p*-bromoanilides of a number of the paraffin acids. The most comprehensive list of such p-bromoanilides which appears in the literature is that reported by Robertson [Robertson, *J. Chem. Soc.*, **115**, 1210 (1919)]. This list, however, does not contain the derivatives of isobutyric or isovaleric acids.

The procedure used for the preparation of the *p*-bromoanilides of the acids from acetic to stearic is a modification of Robertson's procedure and is as follows: One gram (1 mol) of the acid or its sodium salt was placed in a small flask or test-tube and treated with 1 mol of thionyl chloride and heated under a reflux condenser for thirty minutes. The reaction mixture was then cooled and treated with 2 mols of *p*-bromoaniline in 30 cc. of benzene. After warming on a steam-bath for a few minutes the benzene solution was cooled, transferred to a separatory funnel, washed twice with water, twice with 5% hydrochloric acid, once with 5% sodium hydroxide and finally with water. The benzene solution was then evaporated to dryness and the remaining bromoanilide recrystallized from ethyl alcohol The melting points and analyses of these derivatives of isobutyric and isovaleric acids are

	M. p., °C.	Bromine, %	
		Calcd.	Found (Carius)
p-Bromoisobutyranilide	150–151	33.03	32.43
p-Bromoisovaleranilide	128–129	31.10	31.12

The *p*-bromoisobutyranilide has been reported by Norton [*Am. Chem. J.*, **7**, 116 (1885)] as melting at 128°. Judging from the low melting point

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[1] Finkelstein, *Ber.*, **43**, 1530 (1910).

and satisfactory analysis reported for this p-bromoanilide it is quite probable that it was contaminated with some of the ortho isomer, *as* it was prepared by the bromination of isobutyranilide. *p*-Bromoisovaleranilide **does** not appear to have been described previously in the literature.

Contribution from the
Department of Chemistry
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Madison, Wisconsin

Marguerite Kuehn
S. M. McElvain

Received January 26, 1931
Published March 6, 1931

COMMUNICATIONS TO THE EDITOR

THE α,β,γ-TRIMETHYLGLUTARIC ACIDS

Sir:

In a recent paper Michael and Ross[1] reported the failure to obtain α,β,γ-trimethyl-α-carboxyglutaric acid in a crystalline form. I had obtained this acid[2] and reported it as melting at **144–145'.** Michael and Ross note that 145° is also the melting point of **α,β-dimethyl-γ-carboxy**glutaric acid, which suggests that the two are identical. The fact is that I obtained α,β,γ-trimethylglutaric acid melting at 134° from the decomposition of my acid, whereas α,β-dimethyl-γ-carboxyglutaric acid upon decomposition gives a,@-dimethylglutaric acid melting at 87°.[3]

Michael and Ross obtained α,β,γ-trimethyl-α-carboxyglutaric acid as a sirup which on distillation gave an acid melting at 115–125°. In my work on these compounds I found that it was necessary to obtain the tricarboxylic acid in **a** pure state before decomposing it in order to effect the purification of the **α,β,**y-trimethylglutaric acid. Even so it required ten recrystallizations to reach the melting point of **134'.** The compound which Michael and Ross describe as ***cis*-α,β,**y-trimethylglutaric acid, which according to their statement "softened at 115° and melted at 125°," was probably an impure acid identical with mine, which melted at **134'.** The liquid which they call *trans*-α,β,γ-trimethylglutaric acid was, apparently, the same as the liquid remaining in the mother liquors from the crystallization of the acid melting at 134°. Neither their work nor mine is sufficiently complete to characterize this liquid as a definite chemical individual. Inasmuch as modern theory predicts the occurrence of ***three*** stereoisomeric forms (one racemic and two meso acids) it would, in my opinion, be unfortunate if it should be so described in handbooks.

Michael and Ross attempted to separate their acids into a "cis" and a ***"tram"*** form by converting the "*cis*" form into the anhydride and the imide. Granting free rotation about a single bond *all* three of the possible

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[1] **Michael and Ross, This Journal, 52,4607 (1930).**

[2] **Ray, *ibid.*, *50*, 558 (1928).**

[3] **Thorpe, J. *Chem. Soc.*, 83, 358 (1903).**

compounds should form anhydrides or imides and no direct separation is possible by this method.[4]

Department of Chemistry
University of Cincinnati
Cincinnati, Ohio
F. E. Ray

Received December 1, 1930
Published March 6, 1931

THE α,β,γ-TRIMETHYLGLUTARIC ACIDS

Sir:

In the preceding Communication F. E. Ray expresses the opinion that in our recent paper [This journal, 52, 4598 (1930)] (a) certain compounds described were impure and (b) that the method of separation of the α,β,γ-trimethylglutaric acids was not valid.

With respect to his first objection, we would draw attention to the fact that the compounds we described were analytically pure and, in the cases where crystalline, were unchanged in melting points after the third crystallization.

Ray prepared his tiglic ester through methylethylmalonic ester, obtained apparently by methylation and ethylation of sodium enol malonic ester. Besides the methylethylmalonic ester, the reaction product would contain monomethyl or ethyl and dimethyl or diethyl malonic esters, which cannot be completely separated by fractional distillation [Michael, *J. prakt. Chem.*, 72, 537 (1905)]. Ray finally obtained a product which boiled at 100° (30 mm.), which is clearly too high for tiglic ester (b. p. 156° (760 mm.)). The addition compound he prepared from this product through sodium enol cyanacetic ester boiled at 150–170" (30 mm.) and this obviously impure material was methylated. By hydrolysis the product gave a solid acid from which by repeated crystallization, a 145° melting acid was isolated. This was considered to be a-carboxy α,β,γ-trimethylglutaric

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[4] Since writing this Note, Michael and Ross in a footnote contained in the following Communication to the Editor, p. 1175, have kindly called my attention to a transposition of an analysis in my paper[6] [This journal, 50,562 (1928)]. The silver salt of α,β,γ-trimethyl-α-carboxyglutaric acid was analyzed and found correct (page 662, line 15). Following this is given the titration of the α,β,γ-trimethylglutaric acid, $C_8H_{14}O_4$. This should, of course, have followed the paragraph which describes the preparation of this acid from the malonic acid derivative for which the analysis of the silver salt is given.

In the hope of identifying this α,β,γ-trimethylglutaric acid (m. p. 134°) as the racemic form I have attempted its resolution by means of the brucine and strychnine salts but without success. It may thus be one of the meso forms. As a check to previous work the silver salt of the acid was prepared and analyzed with the following results:

Anal. Subs., 0.0450: Ag, 0.0248. Calcd. for $C_8H_{12}O_4Ag_2$: Ag, 55.6. Found: Ag, 55.1.

This leaves no doubt that the acid melting at 134° is α,β,γ-trimethylglutaric acid.

acid but the formula was not proved by analysis.[1] No yield was given of this acid and it was not clear from the description in his paper that the 145° melting acid was used for pyrogenic decomposition. In his preparation of the tribasic acid through tiglic and sodium enol malonic esters, Ray obtained it as a sirup from which apparently he could obtain the 134° melting dicarboxylic acid more readily than from the 145° melting acid. It is therefore difficult to understand the reference in his letter of "necessity to purify before decomposition." The acid melting at 134° was described as α,β,γ-trimethylglutaric acid, although no analyses of this material are given. We, therefore, cannot attach the importance that Ray does to this substance of unknown composition, obtained from an impure source.

With respect to the second objection, the validity of the method is a well established fact. The stereomeric poly-alkyl dicarboxylic acids do not form anhydrides with equal facility, or of equal stability, and we refer Dr. Ray to the literature of these acids [Perkin and Bone, J. Chem. *Soc.*, 69, 264 (1896); Thorpe and Young, *ibid.*, **83,** 358 (1903), and others].

Since we used this method in the separation of the α,β,γ-trimethylglutaric acids, our products were described as *cis* and *trans* to indicate their origin and relative ease of anhydride formation. It was not relevant to our investigation to separate the possible stereomeric forms of α,β,γ-trimethylglutaric acid; it was sufficient for us to obtain a pure imide, m. p. 90°, and an acid, m. p. 125°, as reference compounds and to indicate further the existence of a *trans* acid form.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

ARTHUR MICHAEL
JOHN ROSS

RECEIVED DECEMBER 18, 1930
PUBLISHED MARCH 6, 1931

STEREOCHEMISTRY OF DERIVATIVES OF DIPHENYL AND ANALOGS

Sir:

Apparently the first suggestion that stereoisomerism of the type observed in the diphenyl series might also occur among binuclear heterocyclic aromatic substances is due to Kermack and Slater,[1] who attempted the resolution of 3-o-nitrophenyl-indole-2-carboxytic acid. A recent publication by Steele and Adams[2] describes the attempted resolution of certain phenylpyridine compounds.

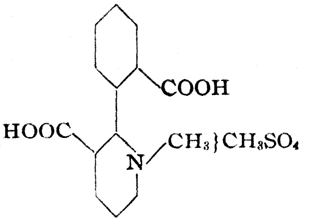
[1] Ray gives no C and H analysis of this acid. Using very small quantities of material he showed by analysis of the silver salt that the silver content agreed with the formula of a tricarboxylic acid $C_9H_{14}O_6$, but titration with 0.1 N alkali indicated a dicarboxylic acid $C_8H_{14}O_4$. Analysis of the silver salt and titration could only indicate the equivalent of the acid. These conflicting analyses cannot indicate whether the acid was methylated; that is, whether the acid was $C_9H_{14}O_6$ or $C_8H_{12}O_6$.

[1] Kermack and Slater, *J. Chem. Soc.*, **36 (1928)**.

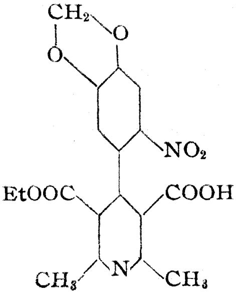
[2] Steele and Adams, THIS JOURNAL, 52, 4528 (1930).

An extensive investigation of such heterocyclic substances as might be expected to exhibit stereoisomerism of diphenyl type has been in progress in these laboratories for some time, but owing to failure to obtain the substances examined in enantiomorphous forms up to the present, publication of results, with the exception of an introductory paper by Chalmers, Lions and Robson,[3] has been so far withheld.

In the 2-phenylpyridine series and the 2-phenylquinoline series attempts have been made to provide a "blocking group" by conversion of the tertiary nitrogen atom into a quaternary salt. Thus, 2-(-o-carboxyphenyl-)-3-carboxypyridine methosulfate (I) has been examined. but its resolution not effected.

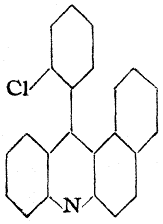


I

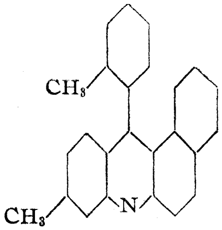


II

Derivatives of 4-phenylpyridine such as (II) have been prepared by the Hantzsch synthesis, and attempts at resolution are in progress. It is worthy of note in this connection that ortho-substituted benzaldehydes react least readily in the Hantzsch synthesis.[4] In the isoquinoline series 1-(-*o*-chlorophenyl-)-isoquinoline methiodide and ethiodide, and 1-(-a-tolyl-)-isoquinoline methiodide and ethiodide have been prepared and converted into the corresponding salts of optically active acids, but these are apparently homogeneous. The acridine compounds (III) and (IV) have also been prepared and examined but not separated into enantiomorphs.



III



IV

This consistent failure to resolve **a** compound of the phenylpyridine series suggests that the conditions there obtaining are different from those in the diphenyl series, probably owing to the definitely polar character of

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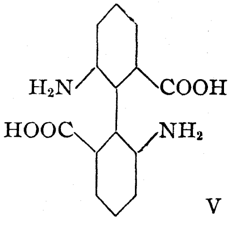
[3] **Chalmers, Lions and Robson, J. Roy.** ***Soc. New South Wales*** **(1930).**

[4] **Hinkel and Madel, J.** ***Chem. Soc.,*** **750 (1929).**

the pyridine nitrogen atom. Undoubtedly, there would be a powerful attraction between this atom and an ortho carboxyl of the benzene ring, leading to pronounced molecular distortion. As yet, the resolution of a derivative of diphenyl having strongly positive groups in the 2,2′-positions and strongly negative groups in the 6,6′-positions has not been effected. 2,2′-Diamino-6,6′-dicarboxydiphenyl (V) passes immediately on its formation into the dilactam (VI).[5] Presumably, in this substance both pyridone rings lie in the same plane as the benzene rings, though this has not definitely been established.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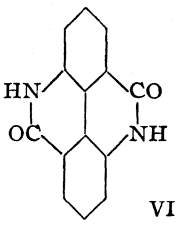
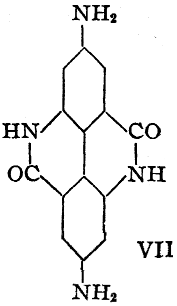
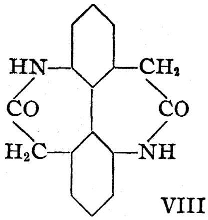
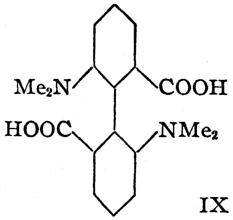
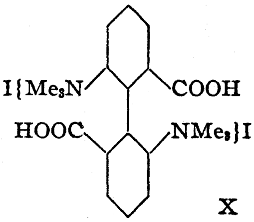

VI


VII

At present the optical homogeneity of (VII) is under examination. It is also proposed to attempt the preparation and resolution of ring homologs of (VI), *e.* g., the dilactam (VIII) in which the benzene rings should lie out of one plane, two configurations thus being possible. Further attempts to resolve 2,2′-tetramethyldiamino-6,6′-dicarboxydiphenyl (IX) and 2,2′-hexamethyldiamino-6,6′-dicarboxydiphenyl dimethiodide (X) and the corresponding betaine (XI) are in progress. The behavior of all these substances may shed some light on the phenomenon in the phenylpyridine series.


VIII


IX


X

Finally, the examination of certain phenylpyrroles and phenylindoles is in progress. According to the obstacle theory it is to be expected that in such binuclear systems the smallest groups which would be effective in preventing free rotation of the nuclei about their common axis must be larger than in the diphenyl series. Hence, the first example chosen for study which is expected to be resolvable is 1-(-*o*-xenyl-)-2,5-diphenylpyrrole-3-carboxylic acid (XII).

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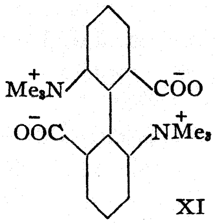
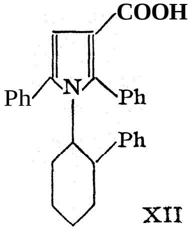
[5] Cf. Kenner and Stubbings, *J. Chem. Soc.*, **119**, **593** **(1921)**.


XI


XII

DEPARTMENT OF ORGANIC CHEMISTRY
THE UNIVERSITY OF SYDNEY
NEW SOUTH WALES, AUSTRALIA
FRANCIS LIONS

RECEIVED JANUARY 27, 1931
PUBLISHED MARCH 6, 1931

THE CRYSTAL FORM OF NICKEL OXIDES

Sir:

In making adsorption measurements of carbon dioxide on nickel oxide, it was found by one of us[1] that the adsorptive properties of the oxide varied quite markedly for different modes of heat treatment.

The nickel oxide was prepared by oxidation of suspended nickelous hydroxide with chlorine gas in basic solution. The black precipitate of the oxide was electrolyzed free of alkali and dried. One sample was outgassed several times at 285°, while the other was not subjected to a temperature of more than 110°.

The first preparation was the poorer adsorbent for carbon dioxide. The adsorption was carried out at 56.5° and the amounts adsorbed were in the approximate ratio of 1:2.5.

This difference of behavior, which was unlikely due to sintering, since the overheated form had rather smaller particle size as indicated by the line-width of the x-ray diagrams referred to below, also could not be explained on the basis of chemical differences, since in the Bunsen test for higher oxides, only traces of such could be found in either case. Both samples corresponded to nickelous oxide.

The substances were then subjected to x-ray analysis by means of the Debye–Scherrer–Hull method.

The overheated oxide corresponded exactly to the previously reported structure for nickelous oxide, being face-centered cubic. The edge of the unit cube was found to be 4.14 Å. (uncorrected), which corresponds to 4.17 Å. as given by the "International Critical Tables."

The structure of the nickelous oxide which had not been heated above 110° was quite different. Although also cubic, the edge of the unit cube was 4.64 Å. (uncorrected). The density was determined as 4.8 as compared to 6.69, given as the density of the ordinary nickelous oxide (Landolt–Bomstein "Tabellen"). The number of molecules in the unit cell

[1] O. G. Bennett, "Thesis," The Johns Hopkins University, 1930.

was calculated as four, with the same accuracy as for the known oxide. However, from a consideration of the intensities of reflection, the face-centered cubic type is not permissible. The complete determination of the atomic coordinates has not been finished as yet.

This form also differs from the ordinary nickelous oxide by causing an unusual amount of fogging on the photographic film when a Debye-Scherrer diagram is taken (Fe-radiation).

Evidently we have found a new cubic modification of nickelous oxide; we have also some evidence for the existence of further modifications. The possibility of the existence of several modifications of nickelous oxide is indicated by the work of Hedvall [Z. *anorg. Chem.*, *92*, 381 (1915)].

This work is being continued and special emphasis is laid on the determination of a possible relation between adsorption, catalysis and structure.

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

O. G. BENNETT
R. W. CAIRNS
EMIL OTT

RECEIVED JANUARY 28, 1931
PUBLISHED MARCH 6, 1931

THE FREE ENERGY OF PORMATIOR OF THALLIUM AMALGAMS

Sir:

Recently Tammann has reviewed the subject of heterogeneous equilibria both from the theoretical and the practical standpoint.[1] Besides describing the different types of phase diagrams, he shows how they can be derived from purely thermodynamic considerations, using the surfaces in free energy (*F*)-temperature-composition space taken for the several phases. Successive isothermal planes cut the F-surfaces in curves which define the singular points on isothermal lines across the phase diagram.

These surfaces, however, give only form and characteristics of the general types of diagrams, and have not been applied to any specific systems, since absolute values of F, which are needed for the calculation, have not been obtained, although changes of the free energy are easily measurable.

Nevertheless I believe I have succeeded in calculating a curve for the system thallium–mercury which represents the general form of the intersection of the free energy surfaces for that system with the 20° isothermal plane. I have calculated the free energy of formation of thallium amalgams from the elements, using the data of Richards and Daniels,[2] Lewis and Randall,[3] and Richards and Smyth[4] by a method which I will explain

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[1] Tammann, "The States of Aggregation," translated by Mehl, D. Van Nostrand Co., New York, 1925; Tammann, "Metallography," translated by Dean and Swenson, The Chemical Catalog Co., New York, 1925; Tammann, "Lehrbuch der Heterogenen Gleichgewichte," Vieweg and Son, 1924.

[3] Richards and Daniels, THIS JOURNAL, 41, 1732 (1919)

[3] Lewis and Randall, ibid., 43, 233 (1921).

[4] Richards and Smyth, *ibid.*, 44, 524 (1922).

in detail in the full report. Briefly, the free energy of formation is a linear function of the mole fractions and partial molal free energies of thallium and mercury in amalgamated and free states. If the last-named quantities—partial molal free energies of solid thallium and liquid mercury—were known, the true F-curve could be drawn; they are, however, constants at any given temperature, and enter my equations as products by the first power of the mole fraction, hence the only effect on the F-curve is to subject it to that type of linear transformation known as a "shear." While a "shear" will change certain features of a curve, such as slope, certain other features, in this case more important, are unchanged. The curve is presented (Fig. 1).

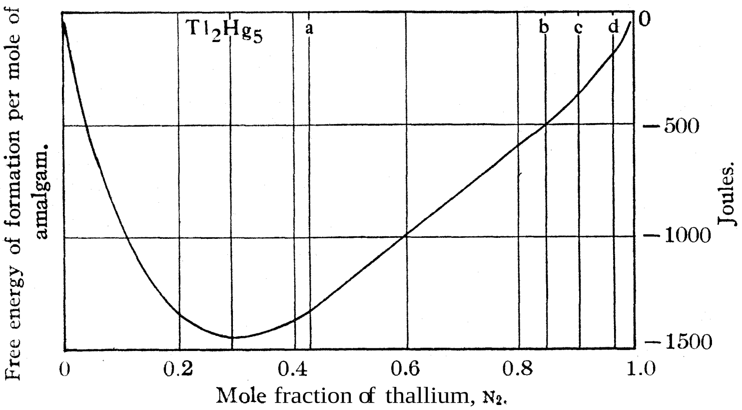


Fig. 1.—Free energies of formation of thallium amalgams

The parts of the curve included between the vertical lines *a* and b, and *c* and d are straight lines, and will remain straight lines after a shear. Straight lines are to be expected, representing the common tangent to the free energy curves of the two phases in equilibrium in these regions. There is also a minimum at $N_2 = 0.285$ which is not to be expected from Tammann's treatment. It coincides, however, with the composition of the known compound Tl_2Hg_5. The appearance of this minimum is all the more surprising since no singular point appears in the e. m. f. curve at this composition, and 20° is five degrees above the melting point of the compound, so that we have it existing in solution only.

Complete details of the method and calculations will be presented in an article to be submitted shortly.

Research Laboratory of
Inorganic Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts

Charles Edwin Teeter, Jr.

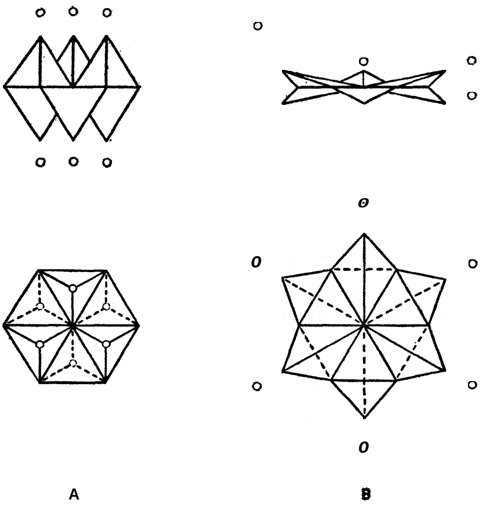
Received February 10, 1931
Published March 6, 1931

THE OSCILLATING, PUCKERED, CENTROID MODEL FOR THE BENZENE RING

Sir:

Some time ago[1] the writer showed that many of the peculiarities of benzene and its derivatives could be accounted for by assuming a structure for the ring like that postulated by Körner[2] (Fig. 1, A) except for distorted (B) rather than regular tetrahedra. (The tetrahedra represent assumed preferred orientations of valence electrons or orbits.)[3]

The chief argument against this structure was lack of evidence for isomers which would be expected of disubstituted benzene derivatives. It has since been shown[4] that predictions on the basis of that theory that so-called 1,8-disubstitution products of naphthalene would be found to be 1,5-, and vice versa, are incorrect. Moreover, x-ray studies of graphite[6] and of $C(CH_3)_6$[6] have indicated that in these substances the **centers** of the carbon atoms, of a single layer or molecule, lie in or nearly in one plane.



This evidence is satisfied if one assumes that the "tetrahedra" are sufficiently distorted, placing 1,8-substituents in naphthalene closer together than 1,5-substituents, and that there is frequent or constant oscillation between such a puckered form and its mirror image, preventing the isolation of isomers and giving a time-average distribution of x-ray scattering power ("electron density") like that deduced from the observations.

Consideration of such forces as the repulsion between atomic kernels would lead one to expect a tendency toward a puckered rather than a plane ring. With only slight puckering the same factors which are responsible for molecular rotation in the solid state[7] might be expected to

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[1] Huggins, THIS JOURNAL, 44, 1607 (1922).

[2] Korner, *Gazz. chim. ital.*, *4*, 444 (1874).

[3] Cf. Bartlett, *Phys. Rev.*, 36, 1096 (1930), and papers by Bartlett and by Slater at the Cleveland Meeting of the American Physical Society.

[4] Fuson, THIS JOURNAL, 46, 2779 (1924); 47, 2018 (1925).

[5] Hassel and Mark, Z. *Physik*, 25, 317 (1924); Bernal, *Proc. Roy. Soc.* (London), **A106**, 749 (1924).

[6] Lonsdale, *Proc. Roy. Soc.* (London), **A123**, 494 (1929).

[7] Pauling, *Phys. Rea*, 36, 430 (1930).

produce the type of oscillation suggested. At sufficiently low temperatures this oscillation should cease. One would expect, therefore, small "humps" in the heat capacity curves of all benzene derivatives (unless oscillation is prevented by external forces), similar to those found[8] for certain of them which have been attributed' to rotation of CH_3 groups.

Another alternative is to assume easy (not necessarily frequent) oscillation and that the orientation of the puckering in a particular molecule in crystalline $C(CH_3)_6$ does not depend on the orientations in surrounding molecules.

The "anomalous" isomerism found among biphenyl derivatives may perhaps be due to non-oscillating puckered rings, rather than to a lack of free rotation about the bond joining them.

X-Ray studies have revealed no cases of two mutually perpendicular planes of symmetry passing through benzene ring centers (as would be expected if the rings were plane), although in several cases a center of symmetry has been found.[9] X-Ray evidence also definitely favors models with equivalent atoms at or oscillating about the corners of a regular hexagon. A satisfactory model must account, moreover, for the synthesis of benzene derivatives, first by methods indicating 1,4-linkages and second, by simple ring closure of a conjugated system.[10] The writer knows of no model, other than that proposed here, which meets these requirements.

From this model one would predict that "electron density" calculations from accurate x-ray intensity data by the method of Fourier Series summations[11] would show the carbon atom "peaks" to be considerably elongated normal to the "plane of the ring."

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA
MAURICE L. HUGGINS

RECEIVED FEBRUARY 11, 1931
PUBLISHED MARCH 6, 1931

GRADUAL TRANSITION IN CRYSTALLINE SODIUM NITRATE[1]

Sir:

Some interest has been elicited in recent years in gradual transitions in crystalline solids. In these transitions the heat capacity of the crystal alters abnormally over an extended range of temperatures, with a more or less well-defined temperature at which the heat capacity reaches a maxi-

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[8] Huffman, Parks and Daniels, THIS JOURNAL, 52,1517 (1930).

[9] See, for instance, Hendricks, Chem. Rev., 7,431 (1930).

[10] Ingold, J. Chem. *Soc.*, *121*, 1143 (1922).

[11] Duane, *Proc. Nat.* Acad. *Sci.*, 11, 489 (1925); Havighurst, *ibid.*, 11, 502 (1925); Compton, "X-Rays and Electrons," D. Van Nostrand *Co.*, Inc., New York, 1926, p. 151; W. L. Bragg, *Proc. Roy. Soc.* (London), A123, 537 (1929).

[1] Abstract of a presentation made at the February meeting of the Washington Section of the American Chemical Society, Washington. D. C.

mum, but there is no sharply defined finite discontinuity in the total heat absorbed. All the examples quoted in the literature (see, *e.* g., the work of F. Simon on ammonium salts, Giauque and Wiebe on hydrogen bromide and iodide, K. Clusius on crystalline nitrogen, oxygen, methane, etc.) occur in the region of very low temperatures, and are for this reason difficult to examine for changes in other physical properties. There exists accordingly some uncertainty as to the exact behavior of a crystal during these apparent inversions, and doubt has been expressed [A. Smits, *Physik. Z.*, (1930)] as to whether the experimental conditions do not account for the anomaly. It is also clear that theoretical explanations of this type of transition [L. Pauling, *Phys. Rev.*, August (1930)] cannot be fully accepted for all cases until our knowledge is more complete.

Sodium nitrate exhibits a gradual transition which ends at approximately 275°. We have examined the changes in heat capacity as shown by differential heating and cooling curves, thermal expansion, the solubility of the salt to its melting point in water, and the x-ray diffraction patterns at various temperatures. Further work on other properties is in progress. The results obtained indicate that the properties of sodium nitrate crystals alter reproducibly over a range of temperatures rather than suddenly at a definite transition point. The expansion coefficient is nearly constant to about 150°, then it gradually increases to a peak value near 275°, followed by a rapid decrease to a normal value beyond 280°. The heat absorption on heating likewise gradually increases to a maximum at 275.5°, while on cooling the heat evolution begins at about 278°. Hysteresis phenomena are completely absent. The change in x-ray patterns is definite but small, and optical examination with a heating microscope shows that the crystals remain optically uniaxial up to the melting point. The solubility curve undergoes a small, but apparently real, change in the transition region. The detailed results of the experimental work will be communicated in the near future.

THE GEOPHYSICAL LABORATORY
CARNEGIE INSTITUTION OF WASHINGTON
WASHINGTON, D. C.

F. C. KRACEK
E. POSNJAK

RECEIVED FEBRUARY 16, 1931
PUBLISHED MARCH 6, 1931

THE PHOTO-REACTION BETWEEN HYDROGEN AND IODINE MONOCHLORIDE

Sir:

In a note on the reaction between iodine monochloride and hydrogen, D. P. Mellor and T. Iredale[1] have presented some experiments which they believe are contrary to conclusions presented by us in a recent paper.[2]

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[1] Mellor and Iredale, Nature, 127, 93 (1931).

[2] Rollefson and Lindquist, THIS JOURNAL, 52, 2793 (1930)

We wish to call attention to the fact that their experimental results are not a contradiction of ours, as the conditions were considerably different, and furthermore their results may be interpreted in a manner consistent with our conclusions.

In the first place if we have a group of normal chlorine atoms formed, approximately 2% of them should in time acquire the energy of activation to the $^2P_1$ state by collisions. These atoms would be capable of forming hydrochloric acid by reaction with hydrogen. If, however, the atoms were destroyed by a reaction such as $ICl + Cl = Cl_2 + I$ before they acquired this energy, there would be no hydrochloric acid formation. Therefore, the most favorable conditions for reaction with hydrogen would be with the hydrogen pressure much higher than the iodine monochloride pressure. Mellor and Iredale had this condition in that they had the hydrogen' pressure approximately forty times that of the iodine monochloride, whereas in our experiments of this kind the two pressures were of the same magnitude. Our results were confirmed by Franck and Rabinowitsch,[3] who found no reaction between hydrogen and iodine monochloride when they used an electric spark for excitation.

Mellor and Iredale apparently missed the principal point of our argument, namely, that in a given mixture of iodine monochloride, chlorine and hydrogen, light absorbed by the chlorine started a reaction whereas that absorbed by the iodine monochloride did not. That experimental fact is definite proof that the action of light on chlorine gives a product different from that resulting from iodine monochloride. This point is discussed in detail in our previous paper.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
G. K. ROLLEFSON
F. E. LINDQUIST

RECEIVED FEBRUARY 16, 1931
PUBLISHED MARCH 6, 1931

THE REMOVAL OF HYDROGEN HALIDE FROM ORGANIC HALIDES

Sir:

In view of the recent appearance of an article by Semb and McElvain [THIS JOURNAL, 53, 690 (1931)] on the reaction of organic halides with secondary amines, we should like to state that we have been investigating the reaction of organic halides with tertiary amines with the hope of using this reaction to determine the relative ease of removal of hydrogen halide from various organic halides. From the work of Semb and McElvain it is apparent that the usual course of the reaction of organic halides with secondary amines, and in particular with piperidine, is the formation of tertiary amines and that the removal of hydrogen halide takes place to a considerable extent only from tertiary halides. In our work using

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[3] Franck and Rabinowitsch, *Z. Elektrochem.*, 36,794 (1930).

tertiary amines, and in particular pyridine, the main reaction other than quaternary salt formation appears to be the removal of halogen acid, although rearrangement of the quaternary salt to alkyl pyridine hydrohalides has not been excluded. We have used direct titration with standard alkali to determine the extent of elimination of hydrogen halide and have followed the rate of this reaction for a number of alkyl halides. We hope to be able to publish our results shortly.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIFORNIA
C. R. NOLLER
R. DINSMORE

RECEIVED FEBRUARY 24, 1931
PUBLISHED MARCH 6, 1931

CALCULATIONS ON THE VELOCITY OF SOUND IN NITROGEN TETROXIDE

Sir:

In a recent publication, Kistiakowsky and Richards[1] describe an attempt to determine the velocity of the dissociation of nitrogen tetroxide from measurements of the velocity of sound in the gas at 25° and various pressures. Their experimental curve for the change in velocity with pressure is not in good agreement with that calculated from the equation of Einstein[2] giving the velocity of sound in a dissociating gas at frequencies below the critical frequency. Kistiakowsky and Richards attribute the deviation to the inaccuracy of the dissociation data of Bodenstein[3] used in the calculations.

In a forthcoming publication, we report new data on the dissociation of nitrogen tetroxide; we have substituted these data in the theoretical equation and compared the result with the curves of Kistiakowsky and Richards. Einstein's derivation assumes that the gas in question is a perfect gas; this is obviously not true for nitrogen tetroxide. Since we have the pressure coefficient of the equilibrium constant, which varies at 25° according to the equation

$$K_p = 0.1426 - 0.7588\, C^0_{N_2O_4}$$

where

$$C^0_{N_2O_4} = \frac{\text{weight of } (N_2O_4 + NO_2)}{92.02}$$

we can calculate, for any given pressure, the deviation from the ideal condition. Further, from our extrapolation to zero pressure, we have a new value for the heat of dissociation—13,960 calories per mole at constant volume. In making the calculations, we have accepted the values assumed by Kistiakowsky and Richards for the specific heats of nitrogen tetroxide and nitrogen dioxide.

We have plotted the velocity of sound, $V_{\text{theoretical}}$, as calculated from

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[1] Kistiakowsky and Richards, THIS JOURNAL, 52, 4661 (1930).

[2] Einstein, *Sitzb. Berl. Akad.*, 380 (1920).

[3] Bodenstein, *Z. physik. Chem.*, 100, 68 (1922).

our dissociation data, on a graph similar to that given by Kistiakowsky and Richards on page 4666 (Reference I). The differences between this curve and the curve representing the direct experimental measurements of Kistiakowsky and Richards $V_{\text{experimental}}$ are given in the second column of the following table. In the last column are given the differences based on Bodenstein's data without the pressure corrections for the equilibrium constant.

Pressure in mm.	$V_{\text{experimental}} - V_{\text{theoretical}}$ (in meters/sec)	
	Verhoek and Daniels	Bodenstein
200	2.9	2.2
300	3.0	1.2
400	2.9	0.7
500	2.4	.1
600	1.9	− .3
700	1.5	− .7

While the agreement between the experimental curve and the theoretical curve can hardly be said to be any better using our data, the deviation is nearly constant, and the calculated velocity is always less than the observed velocity. This fact seems to indicate some constant error, either in theory or experiment. In the derivation of Einstein it is assumed that the gas is only slightly absorbing and that the dissociation proceeds according to a unimolecular reaction. It is possible that these assumptions are not sufficiently well satisfied.

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

FRANK VERHOEK
FARRINGTON DANIELS

RECEIVED FEBRUARY 24, 1931
PUBLISHED MARCH 6, 1931

NEW BOOKS

Periodisches System. Geschichte und Theorie. (Periodic System: History and Theory.) By DR. EUGEN **RABINOWITSCH,** Gottingen, and DR. ERICH **THILO,** Berlin. Verlag von Ferdinand Enke, Stuttgart, Germany, 1930. **xii + 302 pp. 50** ***figs.*** 16.5 X 24.5 cm.

This is a textbook which takes up the periodic system both from a chemical and physical point of view. It is a welcome addition to our list of textbooks as it collects in one place a considerable amount of related material of great importance to the chemist who is at all interested in theoretical things, and which, as far as the reviewer is aware, has not previously all been brought together in one place in textbook form. It is to be recommended for advanced students of chemistry who wish to (or ought to) learn something about quantum theory (even though it be mostly old quantum theory) and its applications, without wading through too much material of a highly mathematical character. But many people to whom most of the material is already familiar will undoubtedly be glad to find it assembled in simple and readable form, though to them the inclusion of references to original sources would have greatly increased its value.

The book is divided into five parts. The first part is an historical treatment of the ideas leading up to the development of the periodic system. This seems to the reviewer to be very useful, inasmuch as it brings forth clearly the difficulties by which early chemistry was beset (and which are often the student's difficulties) and the methods by which these difficulties were straightened out. The second part treats of electrons, protons and the way they combine to build up nuclei. The fundamental experiments are briefly presented and discussed. The next part takes up the Bohr theory of the atom, and considers the energy states both of hydrogen and the more complicated atoms, the various types of coupling of electrons, the Pauli exclusion principle, etc., and ends with a chapter on wave mechanics. The mathematics is kept to a minimum, and on the whole it is quite clearly written. The fourth part deals in detail with the building-up of the periodic system and the energy diagrams of individual atoms. The fifth part consists of a discussion of the periodicity of the chemical properties of the atoms, and takes up such topics as the Born–Haber cycle, polar and non-polar compounds, etc. It contains much valuable material in tabular form (as do, indeed, other parts of the book). Particularly suggestive is the attempt to calculate the existence limits of ionic compounds, though some of the assumptions involved seem hardly tenable. For example, the reviewer can hardly see how the radius of the ion Ca^+, in a crystal, could be smaller than that of Ca^{++}, but it looks possible that the final results of the calculation would not be much altered if more reasonable values for some of the ionic radii were taken instead of those used by the authors.

There are some misprints in the mathematical portions, and in the lettering of Figs. 43, 46, 48 and 49; on p. *255* "endotherm" is written once for "exotherm." The typography would have been more attractive if italics had been used for mathematical symbols, and it would have been easier to distinguish between *l* and 1.

OSCAR K. RICE

The Study of Crystals. A General Introduction. By T V. BARKER, Fellow of Brasenose College, Oxford. Thomas Murby and Co., 1 Fleet Lane, Ludgate Circus. London E. C. 4, England, 1930. xvi + 137 pp. 195 figs. 15.5 × 25.5 cm. Price, 8/6 net.

The text is accompanied by exercises, descriptions of experiments, and excellent illustrations. Parts of the book on geometrical and physical properties may be used as an elementary laboratory manual; other parts, including the following topics, may be read with profit by more experienced students: crystallization from jellies, space-lattice theory, x-rays, polymorphism, "liquid crystals," isomorphism, equilibria between liquid and crystal phases (this general topic occupies about one-fifth of the book and includes such subjects as reciprocal salt pairs, the microscope as a check on crystallization, mixed-crystals, isodimorphous phases).

Hardness, birefringence and optical orientation are not discussed,

H. E. MERWIN

Systematic Crystallography: An Essay on Crystal Description, Classification and Identification. By T. V. BARKER, Fellow of Brasenose College, Oxford. Thomas Murby and Co., 1 Fleet Lane, Ludgate Circus, London E. C. 4, England, 1930. xi + 115 pp. 76 figs. 16 × 25.5 cm. Price. 7/6 net.

An account is given of a method, which seems as simple as possible, for treating the angular measurements of crystals so that determinative tables can be constructed by listing a minimum number of interfacial angles.

Only slight burdens would be imposed upon describers of new crystals, but the time-consuming task of completing the tables "seems to be a matter for cooperation, personal and financial, and any suggestions toward its fulfilment would be very welcome." The tables will require that many crystals be reoriented and/or have their axial ratios changed. Transformations are based upon the principle of simplest indices, and the pseudo-tetragonal and pseudo-cubic rules.

Appendices contain useful formulas, tables of tangents and multiple tangents, and stereographic nets of 1 and $2^1/_2$ in. radii.

H. E. MERWIN

Chemische Thermodynamik. Einführung in die Lehre von den chemischen Affinitäten und Gleichgewichten. (Chemical Thermodynamics. Introduction into the Study of Chemical Affinities and Equilibria.) By DR. HERMANN ULICH, Professor at the University of Rostock. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1930. xvi + 353 pp. 30 figs. 15.5 × 23.5 cm. Price, unbound, RM. 18.50; bound, KM 20.

In the February, 1930, number of THIS JOURNAL I reviewed a textbook on Thermodynamics by Schottky, Ulich and Wagner. One of the two chemists among the three authors has now written a much simpler text for students interested in the chemical applications, based on the same principles.

These principles are: Consider first the reaction, and build it up from elementary reactions. Then it is only necessary to know the thermodynamical data for these standard elementary reactions. A second step taken in the latter part of the book, is to build up the data of the elementary reaction from data of the substances concerned in it

Other innovations of the book, taken over from the larger work, are the use of the concept of "resistant groups" instead of molecules, especially useful in mixtures with dissociation and association, and the systematic use of "partial" quantities, extended further than by Lewis and Randall.

The outstanding advantage of the book to my mind, however, is that it is the only one that familiarizes the reader both with the American and with the German method of calculating free energies. The former, which is due to Lewis, gives for every substance the entropy at room temperature and needs therefore only relatively small corrections for other temperatures to be made with the help of the specific heats. The German method starts for every solid pure phase with the absolute zero and the Nernst theorem, integrating the specific heats from zero up. This procedure is more fundamental, but much more cumbersome and subject to inaccuracies.

The book contains a comprehensive table of the thermodynamical data of standard reactions.

It is written in an agreeable style and can be well recommended as a textbook. Sometimes the wish to make the book readable seems to have induced the author to use not quite accurate expressions. There is one error, however, in the statement on page 187 that the identity of energy and free energy at the absolute zero is not self-evident, because the entropy might become infinite. This is, however, multiplied with T and it would take an infinite specific heat, which is most unlikely, to overcome this.

K. F. HERZFELD

A Textbook of Organic Chemistry. By A. F. HOLLEMAN, Ph.D., LL.D., D.Sc., F.R.S.E. **Seventh English edition, completely revised with the coöperation of the author. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1930. xx + 594 pp. Illustrated. 15.5 X 23.5 cm. Price $3.50.**

A recent musical comedy advises us that "50 million Frenchmen can't be wrong." Be that as it may, it is more than equally safe to assume that when the editions of a book reach the 50's, and this is one of the 52nd, there must be a great deal that is right about it.

The seventh English edition of Holleman's excellent text not only upholds the high standard of its predecessors, but has been revised to include such recent advances in organic chemistry as Haworth's work on the sugars and Robinson's on strychnine. As no pearl is flawless, so no text, to a reviewer, is quite perfect. It is regrettable that in using the Geneva system, two naming schemes have been introduced. Also some may take exception to the author's usage, consistent though it be, of numbers instead of Greek letters, to designate positions of substituents on carbon chains. All the numerous diagrams do not, unfortunately, depict the best modern laboratory technique. No explanation appears for the term fire-damp, and the writer is led to wonder what students think this term means anyway. The element, now generally called beryllium, is unfortunately designated by a less satisfactory name. Nitriles are always called carbonitriles, but with no seemingly adequate reason, and the term saponification, which should be reserved for the alkaline hydrolysis of esters, is too loosely used. It is rather surprising, considering the generally superior quality of this book, that the *trans* shift in the Beckmann rearrangement is not mentioned, and that Paneth's work on free methyl and ethyl is ignored. The possibility of replacing nuclear halogen to give phenol, likewise is not mentioned. The rather objectionable term disodium malonic ester is employed without indicating that it is merely a convenience and is not to be taken literally. The suggested mechanism for the addition of sodium phenolate to a certain acetylenic compound seems to pay too little attention to the effects of conjugated unsaturation; while the formula for carotene does not agree with that which is commonly assigned to this hydrocarbon.

However, to more than offset the points just taken exception to, mention should be made of the splendid correlation between physical and organic chemistry, to the part given to alicyclic compounds, of the unusually good presentation of the carbohydrates, and of the treatment of the Walden inversion. The Svedberg molecular weight method for proteins is described, and the formula for that interesting substance thyroxine is included. Furthermore, there appears a good account of the low temperature distillation of coal.

This volume is, without doubt, one of the best one-volume texts available. It is meaty, but it is digestible.

G. ALBERT HILL

Neuere Torfchemie. (Modern Peat Chemistry.) By PROF. DR. G. STADNIKOFF. Introduction by Wo. Ostwald. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1930. viii + 167 pp. 17 figs. 15.5 × 23.5 cm. Price, unbound, RM. 12.

An industry as old as the preparation of peat for the market for use as a fuel might seem to have but little room for technical improvement, but the author has demonstrated that not only is there much to be done but also that in the last years very notable advance has been made in fundamental knowledge of the chemical and physical relations of peat and of its decomposition products. It might also be assumed that peat has but little immediate interest for the United States since there is but little prospect of any large scale utilization of a low grade fuel. On the other hand, the enormous acreage of peat lands in this country, over 100,000,000 acres, and the fairly large importations of foreign peats, mostly for agricultural uses, together with utilization of considerable domestic peat for purposes other than heating render additions to our knowledge of the properties of peat timely and useful.

The author, who is scientific director for the National Institute for Coal Research at Moscow, has assembled all the pertinent and reliable published data on the water content of peat, the processes and principles of its dehydration, the components of peat and their chemical and physical properties, the bitumen content and its character, the humus content and its components and the liquid products of peat distillation. To this assemblage of data the author has added the results both of technical development and of scientific research in the laboratories of the Soviet jurisdiction during the past ten years. The scientific data are presented for the most part in the form of tables, seventy-seven in number. The whole body of material is clearly presented and discussed without any attempt to develop a particular or personal point of view. In each topic every material advance in scientific knowledge of peat is developed.

On the whole the booklet, small as it **is,** probably presents the most compact and readily accessible body of information available. The text is accompanied by numerous references to the best scientific and technical literature both in Europe and America down to **1930.**

HORACE G. BYERS

Nutrition and Food Chemistry. By BARNARD S. BRONSON, State College for Teachers, Albany, N. Y. John Wiley and Sons, Inc., New York, 1930. viii + 467 pp. 34 figs. 15 X 23 cm. Price, $3.75.

The purpose of this book, as stated by the author in the preface, is to lessen the burden which is carried by human knowledge regarding food and diet due to the mass of accumulated misinformation about this subject. "It is the outgrowth of attempts over a number of years to sift the grain from the chaff in presenting the elements of nutrition and foods to a group of college students with little foundation in physiology and none in organic chemistry." There is a short introductory chapter on "The Organism and its Environment," followed by eighteen chapters covering the following general topics: "Food, and Mechanics of Digestion;" "Chemistry of Digestion;" "Chemical Changes in the Intestine, and Absorption;" "Composition of Foodstuffs," including two chapters on carbohydrates and one covering both fats and proteins; "Fate of the Foodstuffs," two chapters; "Protein Requirement;" "Energy Requirement;" "Inorganic Salts and Acid-Base Balance;" "Vitamins;" "Milk and Milk Products;" "Butter, Oleomargarine, Cheese, Condensed Milk, and Ice Cream;" "Eggs and Meat;" "Vegetable Foods;" "Legumes, Root Crops, and Green Vegetables," and "Fruits." Several appendices cover the subjects of "New York State Milk Standards," "Distribution of Vitamins," in tabular form, "Terms Used in Standardization of Eggs," and tables showing recent analyses of the iron and copper content of foods.

The author has, in general, covered the field in a very clear and pleasing manner, and shows that he has been a very critical student of the many subjects presented. It is perhaps too much to expect a teacher to be absolutely up to date in a field of applied science in which such a large volume of research is being published yearly. Although the author has brought his subject up to the very latest word in certain fields, the book would be benefited by considerable "sifting," as it stands, and will no doubt require considerably more in the future.

A feature of the book which may appeal to many teachers and students is the etymology of many terms, given in footnotes. The book is well illustrated and the text fortified with many valuable tables, taken from numerous sources, all of which are acknowledged.

The author's style is not as uniform as one might wish, suggesting that the various sections of the subject matter were prepared at different times and not re-written for publication. This is borne out by the considerable amount of tautology in the text, which in a few cases has led to diametrically opposing statements.

Although the author has prepared the chemical sections of his text for students with no foundation in organic chemistry, he does not hesitate to introduce structural formulas in the chapters on the composition of carbohydrates, proteins and fats. This may give the text some appeal to students with more advanced chemical training, but the reviewer questions whether it is possible to teach enough organic chemistry in a few pages of text to make heterocyclic structural formulas intelligible to students who have only the most elementary chemical training. Incidentally, the structural formulas for the sugars are not those most generally accepted by biochemists at the present time and the author's explanation of the gamma sugars is hazy.

L. S. PALMER

BOOKS RECEIVED

February 1, 1931–February 15, 1931

JAMES C. MUNCH. "Bioassays. A Handbook of Quantitative Pharmacology." The Williams and Wilkins Company, Mt. Royal and Guilford Aves , Baltimore, Maryland. 958 pp. **$10.00.**

Wo. OSTWALD. "Kolloidwissenschaft Elektrotechnik und Heterogene Katalyse." Sonderausgabe aus den Kolloidchemischen Beiheften. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 113 pp. RM. 5, unbound.

ALFRED RIECHE. "Alkylperoxyde und Ozonide. Studien uber Peroxydischen Sauerstoff." Verlag von Theodor Steinkopff, Kesidenzstrasse 32, Dresden-Blasewitz, Germany. 172 pp. RM. 10, unbound.

ALFRED WAGNER, ALFONS M. BURGER AND F. ELZE, Editors. "Die Riechstoffe und ihre Derivate." Erste Abteilung: Aldehyde der aliphatischen Reihe. Zweite Abteilung: Aldehyde der alizyklischen Reihe. Dritte Abteilung: Aromatische Oxyaldehyde mit gesättigter Seitenkette—Zweiwertige Oxyaldehyde—Äther aromatischer Oxyaldehyde mit gesättigter und ungesättigter Seitenkette—Aroxylaldehyde. Vierte Abteilung: Patentregister—Patentverzeichnis—Autorenregist und alphabetisches Sachregister. A. Hartleben's Verlag, Singerstrasse 12, Vienna, Austria. 1431 pp.

"Tables Annuelles de Constantes et Données Numeriques de Chimie, de Physique, de Biologie et de Technologie." Table des Matières des Volumes I à V. Années 1910 $1922. McGraw-Hill Book Co., Inc., 370 Seventh Ave., New York. 382 pp.

The Journal of the
American Chemical Society

VOL. 53 APRIL, 1931 No. 4

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

OXIDATION–REDUCTION POTENTIALS.
III. THE MERCURIC–MERCUROUS ELECTRODE

BY STEPHEN POPOBP, JOHN ALLEN RIDDICK, VERDA IRENE WIRTH AND
LEE DUDLEY OUGH

RECEIVED AUGUST 6, 1930 PUBLISHED APRIL 6, 1931

Carter and Robinson[1] were the first investigators to study the oxidation–reduction potential of the mercuric-mercurous electrode, using the perchlorates of mercury. They measured a series of cells of the type

$$Hg \mid Hg_2Cl_2,\ N\ KCl \mid 0.1\ N\ KCl\ Hg_2(ClO_4)_2,\ Hg(ClO_4)_2 \mid Pt^{+2}$$

assuming that the error due to liquid junction was negligible. The perchlorates of mercury had previously been used by Ley and Heimbucher[3] and later by Linhart[4] and found suitable for electromotive force measurements as they are soluble, easily purified, highly ionized and do not form complex ions to any appreciable extent.

In a previous investigation on the oxidation–reduction potential of the ferric–ferrous electrode,[5] a method has been given for the determination of oxidation–reduction potentials in which the difficulties due to incomplete elimination of liquid junctions and the lack of precise data on the activity of an ion in the presence of other electrolytes have been reduced to a minimum.

In this investigation measurements were made of the cell

$$Pt \mid Hz,\ HClO_4 \mid HClO_4,\ Hg(ClO_4)_2,\ Hg_2(ClO_4)_2 \mid Pt^+$$

The liquid junction was maintained constant by a Lamb and Larson[6] flowing junction. The reproducibility of such a junction was established by MacInnes and Yeh.[7]

Two sets (A and B) of experimental data are presented. In both sets

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[1] Carter and Robinson, *J. Chem. Soc.*, 128, 267 (1927).

[2] All notations and abbreviations employed in this paper are those found in the "International Critical Tables," 1929, Vol. VI, p. 322.

[3] Ley and Heimbucher, *Z. Electrochem.*, 10, *301* (1904).

[4] Linhart, THIS JOURNAL, 38, 2356 (1916).

[5] Popoff and Kunz, *ibid.*, 51, 382 (1929).

[6] Lamb and Larson, *ibid.*, 42, 229 (1920).

[7] MacInnes and Yeh, ibid.. 43, 2563 (1921).

the concentrations of the perchloric acid were kept the same throughout the cell.

In Set A the ratio of the concentration of the mercuric perchlorate squared to the concentration of the mercurous perchlorate was maintained as near unity as possible. With decreasing concentrations of the mercury salts, within each series, both sides of the cell approach identity, and the liquid junction potential approaches zero. By plotting a function of the potential against the concentration of the mercurous perchlorate and extrapolating to zero concentration of the mercury salt, the liquid junction potentials should also become zero. To obtain the normal oxidation–reduction potential, one must correct for the presence of perchloric acid. By plotting the extrapolated values obtained from the various acidities against the acid concentrations and again extrapolating to zero concentration of perchloric acid, due correction is made for the presence of perchloric acid.

In Set B the concentration of mercuric perchlorate was kept equal to the concentration of the mercurous perchlorate, this procedure enabling one to work with more dilute solutions and to apply the principle of ionic strength. In this set the values of the oxidation–reduction potentials, E' (without any corrections for the activity coefficients), were found to be constant in each acid series although the concentrations of the mercury salts were varied from 0.008 *m* to 0.0005 m. The values of E' in each acid concentration were plotted against the molality of the perchloric acid and the curve extrapolated to zero. In Set B, series VI and VII, the solutions were dilute enough to use the principle of ionic strength and to calculate approximately the activity coefficients. The oxidation–reduction potentials, E'', thus obtained were plotted against the square roots of the ionic strengths and the line extrapolated to zero ionic strength. The two extrapolated values in Set B were checked mathematically using the method of moments[8,9] and the method of the zero sum.[10] The extrapolated values were found to agree very closely with those obtained by the mathematical methods.

Apparatus and Material

1. Cell and Equipment.—Practically the same cell and potentiometric equipment were employed as were used in former studies.[5,11] All e. m. f. measurements were made at 25 ± 0.01°. An Eppley standard cell, No. 30957, the voltage of which was expressed in International volts was used.

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[8] H. L. Rietz, "Handbook of Mathematical Statistics," Houghton Mifflin Co., New York, 1924, pp. 68–70.

[9] Karl Pearson, "On the Systematic Fitting of Curves," Biometrica, 1902, Vol. I. *pp.* 265–303.

[10] Campbell, "The Adjustment of Observations," *Phil.* Mag., 39, 177 (1929); 47, 816 (1924).

[11] Popoff, Riddick and Becker, THIS JOURNAL, 52, **2624** (1930).

2. All water was redistilled from alkaline permanganate in an all-glass still.

3. All perchloric acid was redistilled in an all-glass still under reduced pressure, the first and last fourths being discarded. Air free from carbon dioxide was then passed through the acid to remove any possible trace of free chlorine.

4. Redistilled mercury was passed five times in a fine spray through a mercury purification column containing mercurous nitrate and nitric acid, and then passed three times through a column of distilled water.

5. Mercuric perchlorate was prepared by treating red mercuric oxide with perchloric acid,[12] until the solution was faintly turbid. After filtering, the solution was concentrated in an all-glass vacuum distillation apparatus under about 10 cm. pressure. Glass beads were introduced into the flask to prevent bumping and to serve as a gage to the concentration of the mercuric perchlorate solution. Mercuric perchlorate is very soluble and hence difficult to crystallize. When the density of the solution became such that the glass beads floated, good crystals could be obtained on slow cooling. Crystals produced by fast cooling came out in one solid mass with which it was difficult to work. Slow cooling produced large crystals when a small excess of perchloric acid was present. These crystals could be well drained and were sometimes about 2 cm. in diameter. Several of these large crystals were measured with a contact goniometer giving the angles M M = 120°, and M C = 90°. These indicate crystals in the hexagonal system with the forms $10\bar{1}0$ and 0001. Only the larger crystals could be removed from the solution for examination. Small crystals lose their identity before they can be examined in the air, this being due to the hygroscopic property of the mercuric perchlorate. Crystallization takes place slowly and when complete the glass beads would sink. The supernatant liquid was poured off and the crystals were drained in a centrifuge in special glass centrifuge cups at 800–900 r. p. m. for about twenty minutes. All mercuric perchlorate was at least twice recrystallized.

6. Mercurous perchlorate was prepared by shaking an acidified solution of mercuric perchlorate with an excess of mercury for forty-eight hours at 50". Subsequent analysis in some of the solutions employed showed that the amount of mercuric perchlorate remaining in the solution was negligible. Both mercuric and mercurous perchlorates were kept in dark bottles under an atmosphere of carbon dioxide. The carbon dioxide was passed through silver sulfate solution and cotton before entering the solution.

7. All other chemicals were of the best quality obtainable.

Analytical Methods

All the data for the analyses are given in Table I. Weight burets were used in all titrations.

1. Standardization of Perchloric and Hydrochloric Acids.—The perchloric and hydrochloric acid solutions were standardized against a standard, carbonate-free sodium hydroxide solution, using phenolphthalein as the indicator. The base was standardized against Bureau of Standards potassium acid phthalate. Standardization against potassium acid phthalate had been found to agree closely with the standardization against benzoic acid and against constant boiling hydrochloric acid.[13]

2. Analysis of Mercuric Salt.—The stock mercuric perchlorate solution was standardized by three entirely different methods. The mercuric sulfide method was adopted as the standard.

a. Mercuric Sulfide Method.—A weighed portion of the mercuric perchlorate solution was acidified with 10 cc. of 0.8 *N* perchloric acid and diluted to 75 cc. Hydrogen

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[12] Chikashige, *J. Chem. Soc.*, 63, 1013 (1895).

[13] Popoff and Neuman, *Ind. Eng. Chem., Anal. Ed.*, 2, 45 (1930).

sulfide was passed for ten minutes. The solution was heated to boiling, cooled, then hydrogen sulfide again was passed until precipitation was complete. The precipitate was filtered through a Gooch crucible, washed with alcohol, carbon disulfide and ether. The carbon disulfide was used to remove any sulfur formed in the oxidation of the hydrogen sulfide. Attempts to employ ammoniacal solutions, etc., as recommended by some, failed to give concordant results. Without the carbon disulfide treatment, the results were very concordant among themselves but higher than the calculated employing pure mercuric chloride as the standard. The precipitate of mercuric sulfide was dried at 105° for one hour. Since the activity product constant of mercuric sulfide is very small (4×10^{-54}), no correction for solubility was made.

b. Potassium Iodide Method.—A solution of potassium iodide was standardized against recrystallized c. p. mercuric chloride. Sodium chloride and perchloric acid were added, the former to retard the formation of mercuric iodide, the latter to give identical conditions in the standardization of the iodide solution as in actual determination of the mercuric ion in the stock solution.

c. Thiocyanate Method.—An approximately 0.1 N solution of potassium thiocyanate was standardized against standard silver nitrate solution using ferric alum as the indicator. Perchloric acid was added for the same reason as in 2b.

The precision of the three methods of determining mercuric ion and the comparison between the three methods are given in Table I, 1 and 2.

Considering the precision of the mercuric sulfide method, one may justify its selection as the standard method, especially after the method was checked using c. p. mercuric chloride as the standard. The other methods were employed as an approximation and a check on a more precise method.

3. Analysis of Mercurous Salt.—The mercurous ion in the stock solution of the mercurous perchlorate was determined by two entirely different methods (see Table I, 3).

a. The Gravimetric Method.—In this method the mercury was precipitated as mercurous chloride with sodium chloride. A correction factor for the solubility and volatility on heating of the mercurous chloride was determined by preparing mercurous chloride, treating a weighed portion of the precipitate under conditions similar to those in the analysis and determining the loss in weight. The filtrate, after the mercurous ion had been precipitated, was treated with hydrogen sulfide, but the amount of the sulfide of mercury obtained was negligible. This method did not give very concordant results in some cases, but the average value agreed with that obtained by the electrometric method.

b. The Electrometric Method.—Mercurous perchlorate was added slowly and with stirring to an excess of sodium chloride solution. The excess sodium chloride was then titrated electrometrically with standard silver nitrate, using a silver–silver chloride electrode. The weight ratio between the sodium chloride and silver nitrate had previously been determined electrometrically. The silver nitrate was standardized against potassium chloride which had been recrystallized three times.

4. Acidity in the Mercury Perchlorate Solutions.—The mercuric and mercurous stock solutions contained free perchloric acid. This acid cannot be determined either electrometrically or colorimetrically employing indicators because of the presence of the mercury salts. The mercury was deposited on mercury cathodes using a current of 0.5 ampere and 3 volts, and the total acid was determined by titration with standard alkali solution. A solution of perchloric acid was electrolyzed using the same kind of electrodes (with free mercury in the solution) as in the analysis for acid in the mercury solution. Since the volume ratios between acid and base (Table I, 4) are the same both before and after electrolysis, it may be concluded that the free acid in the salt solutions can be determined after setting free the mercury on electrolysis by titrating with standard alkali. The acidities of the solutions are given in Table I, 5.

5. Preparation of Solutions of Known Concentration.—The stock solutions of acid and mercury perchlorates were employed for preparing, by weight, the various solutions needed for the cells using the proper buoyancy corrections.

TABLE I

ANALYTICAL METHODS

1. Precision of the Three Methods for Mercuric Ion

HgS method HgS per g. of soln., g.	KI method Weight ratio	KCNS method Weight ratio
0.10858	1.074	0.08319
.10853	1.072	.08315
	1.071	.08323
	1.072	

2. Comparison of the Three Methods for Mercuric Ion

Grams of $Hg(ClO_4)_2$ per gram of solution

HgS method	KI method	KCNS method
0.1864	0.1866	1.1858

3 Mercurous Perchlorate, Grams of $Hg_2(ClO_4)_2$ per gram of solution

	Electrometric	Gravimetric
	0.06635	0.06615
	.06638	.06663
	.06631	.06646
	.06633	.06636
	.06639	.06618
Av.	.06635	.06636

4. Volume Ratio of Acid to Base

Before electrolysis	After electrolysis
2.089	2.090
2.087	2.089

5. Acidities of the Mercury Perchlorate Solutions

Solution	Total $HClO_4$ titer	Mercury titer expressed as $HClO_4$	Actual $HClO_4$ titer
$Hg(ClO_4)_2$	0.1099	0.09374	0.01617
$Hg_2(ClO_4)_2$	.06016	.03986	.02030

Experimental Data

Cells of the type

$$\begin{array}{l} \mathrm{Pt} \mid \mathrm{H_2,\ HClO_4} \mid \mathrm{HClO_4,\ Hg(ClO_4)_2,\ Hg_2(ClO_4)_2} \mid \mathrm{Pt}^{+} \\ \quad E_{\mathrm{H}} \qquad\quad E_1 \qquad\qquad\qquad\qquad\qquad\qquad E_a \end{array}$$

were measured. There are three sources of potential in the cell: E_{H}, the potential of the hydrogen electrode; E_a, the potential of the mercuric–mercurous electrode; and E_1, the liquid junction potential.

E_{H} was calculated from the equation

$$-E_{\mathrm{H}} = 0.05915/2 \log (P_{\mathrm{H_2}}/P_{760} \times 1/a\mathrm{H}^{+2}) \qquad (1)$$

$P_{\mathrm{H_2}}$ is the pressure of the hydrogen taken as the barometric pressure, corrected for brass scale, minus the vapor pressure of the acid solutions used. The vapor pressures were computed and taken to be the same as those for hydrochloric acid from the data given in the "International Critical Tables.[14] $a\text{H}^+$ represents the hydrogen-ion activity which was calculated from data of Randall and Young[15] for the mean activity coefficient of hydrochloric acid. Schuhmann[16] states that the mean activity coefficient of perchloric acid may be taken to be the same as that for hydrochloric acid up to one molal. Experimental data, of a somewhat similar nature, show that this conclusion may be correct, at least within the experimental error.

E_a was found from the equation

$$E_a = E_{\text{cell}} + E_H \qquad (2)$$

E_1 cannot be computed at finite concentrations of mercuric and mercurous perchlorates, but if is kept constant in a given cell by a flowing junction.

1. Set A.—In Set A the ratio of the concentration of the mercuric perchlorate squared to that of the mercurous perchlorate was kept equal to one, but the molalities of the mercury salts were varied as shown in Table II. The mercurous ion is considered as a divalent ion.

TABLE II

THE CONCENTRATION OF THE MERCURY SALTS

Cell	Molality of $Hg_2(ClO_4)_2$	Molality of $Hg(ClO_4)_2$
A	0.008100	0.09000
B	.004000	.06324
C	.002000	.04472
D	.001000	.03162

The electromotive force data are given in Table III. The values of E_a in each acid concentration were plotted (Fig. 1) against the molality

TABLE III

ELECTROMOTIVE FORCE DATA (SET A)

Cell	$E_{\text{obs.}}$	$-E_H$	E_a	Cell	$E_{\text{obs.}}$	$-E_H$	E_a
	Series I. 0.4 m $HClO_4$				Series III. 0.1 m $HClO_4$		
A	0.93257	0.03013	0.9024	A	0.96782	0.06440	0.9034
B	.93247	.03013	.9023	B	.96761	.06440	.9032
C	.93206	.03016	.9019	C	.96674	.06438	.9024
D	.93172	.03016	.9016	D	.96602	.06436	.9017
	Series II. 0.2 m $HClO_4$				Series IV. 0.05 m $HClO_4$		
A	0.94959	0.04760	0.9020	A	0.98643	0.08101	0.9054
B	.94933	.04760	.9017	B	.98626	.08101	.9053
C	.94887	.04748	.9014	C	.98593	.08115	.9048
D	.94851	.04749	.9009	D	.98453	.08114	.9034

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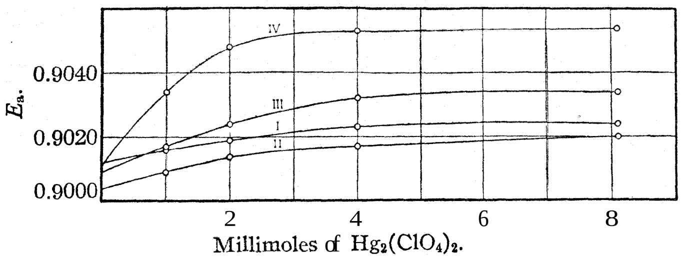
[14] "International Critical Tables," 3, 293 (1928).

[15] Randall and Young, THIS JOURNAL, 50, 995 (1928).

[16] Schuhmann, *ibid.*, 46, 58 (1924).

of the mercurous perchlorate and extrapolated to zero concentration of the mercury salt, eliminating the liquid junction potential. The oxidation–reduction potentials, E', obtained at various acidities are given in Table IV. In Fig. 2 the values of E' were plotted against the molality of the perchloric acid and the curve extrapolated to zero concentration of perchloric acid.



Roman numerals refer *to* series.

Fig. 1.—The oxidation–reduction potentials at various acidities.

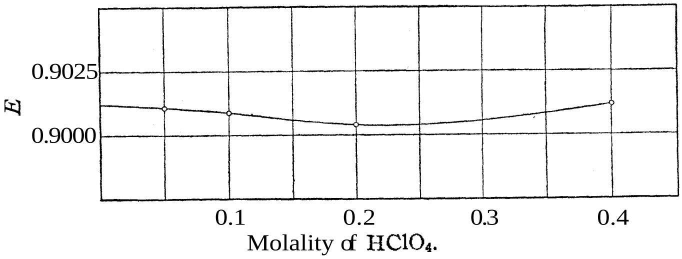


Fig. 2.—The standard oxidation–reduction potential.

TABLE IV

OXIDATION–REDUCTION POTENTIALS AT VARIOUS ACID CONCENTRATIONS

Series	**Molality** of $HClO_4$	E'
I	0.4000	0.9012
II	.2000	.9004
III	.1000	.9009
IV	.0500	.9011

2. Set B.—In Set B the concentration of the mercuric salt was kept equal to the concentration of the mercurous, making it possible to work with a solution in which the ionic strength was as low as 0.023. Table V gives the electromotive force data obtained. E' was calculated from the equation

$$E_a = E' - 0.05915/2\ (\log C_{Hg_2^{++}}/C_{Hg^{++}}^2) \qquad (3)$$

where $C_{Hg_2^{++}}$ represents the concentration of the mercurous ion and $C_{Hg^{++}}^2$ represents the concentration of the mercuric ion squared.

TABLE V

ELECTROMOTIVE FORCE DATA (SET B)

Cell	$C_{Hg^{++}} = C_{Hg_2^{++}}$	$E_{obs.}$	$-E_H$	E_a	E'
		Series I. 1.0 *m* $HClO_4$			
A	0.004	0.84099	0.00471	0.8363	0.9072
B	.0001	.82329	.00477	.8185	.9072
		Series II. 0.4 *m* $HClO_4$			
A	0.005	0.86331	0.03016	0.8332	0.9012
B	.002	.85152	.03016	.8214	.9012
C	.001	.84252	.03003	.8125	.9012
D	.0005	.83300	,03016	.8033	.9010
		Series III. 0.2 *m* $HClO_4$			
A	0.008	0.88644	0.04763	0.8388	0.9008
B	.007	.88465	.04750	.8372	.9009
C	.006	.88275	.04763	.8351	.9008
D	.005	.88014	.04741	.8327	.9007
E	.004	.87722	.04744	.8298	.9007
F	.003	,87371	.04741	.8263	.9009
G	.002	.86828	.04747	.8208	.9006
H	.001	.85949	.04743	.8121	.9008
I	.0005	.85057	.04742	.8031	.9007
		Series IV. 0.12 *m* $HClO_4$			
A	0.006	0.89565	0.06004	0.8356	0.9013
B	.004	.88999	.05986	.8301	.9010
C	.002	.88113	.06004	.8211	.9009
D	.001	.87224	.05986	.8124	.9011
E	.0005	.86321	.05992	.8033	.9009
		Series V. 0.08 *m* $HClO_4$			
A	0.006	0.90598	0.06981	0.8362	0.9019
B	.004	.90087	.06981	.8311	.9020
C	.002	.89167	.06960	.8221	.9019
D	,0005	.87379	.06962	.8042	.9018
		Series VI. 0.04 m $HClO_4$			
A	0.007	0.92644	0.08655	0.8399	0.9036
B	.006	.92424	.08635	.8360	.9035
C	.005	.92189	08648	.8354	.9034
D	.004	.91883	.08635	.8325	.9034
E	.003	.91490	.08642	.8285	.9031
F	.002	.90963	,08635	8233	.9031
G	.001	.90067	.08637	.8143	.9030
H	.0005	,89175	,08642	.8053	.9030
		Series VII. 0.02 m $HClO_4$			
A	0.001	0.91829	0.10331	0.8150	0.9037
B	.0005	.90961	.10331	.8063	.9039

3. **The** Activity Coefficients of **Perchloric** Acid.—Following the procedure of Schuhmann[16] but employing flowing junctions, electromotive force measurements were made using four cells of the type

$$\text{Pt} \mid \text{H}_2, \text{HClO}_4 \mid \text{HCl}, \text{H}_2 \mid \text{Pt}^+$$

The acid concentrations were varied from 0.02 to 1 molal, but the concentrations of the acids in each cell were kept the same. After making corrections for the small variations in concentration and for the liquid junction potentials employing Lewis and Sargent's[17] formula

$$E_1 = -0.05915 \log \frac{\Lambda_{\text{H}^+} + \Lambda_{\text{ClO}_4^-}}{\Lambda_{\text{H}^+} + \Lambda_{\text{Cl}^-}}$$

and the more recent data found in the "International Critical Tables"[18] for the equivalent conductances of the two acids, it was found that any corrections for the unequal activity coefficients of hydrochloric and perchloric acids, would lie within the experimental errors for all concentrations except for the one molal acid, this correction being of the order of 1.2 millivolts.

Final Calculations and Discussion

The standard oxidation–reduction potential of the mercuric–mercurous electrode was finally derived from total concentration and from the principle of ionic strength making use of activity coefficients.

1. From Total Concentration.—It was found convenient in Set **A** to work with solutions in which the concentration of the mercuric salt squared was equal to the concentration of the mercurous salt. By suitable plottings (Figs. 1 and 2), the standard oxidation–reduction potential was found to be 0.9011 volt. By working with solutions in which the concentration of the mercuric perchlorate was kept equal to that of the mercurous, Set B, it was found that when dilute enough solutions were employed, plotting similar to that in Fig. 1 was unnecessary. The average values of E' which correspond to each acid concentration are given in Table VI. Figure **3** gives the curve obtained. The extrapolated value, 0.9050, was checked mathematically using the methods of moments and the zero sum and it was found to be 0.9045.

TABLE VI

VARIATION OF E' WITH ACIDITY

Molality of acid	E'
1.0	0.9072
0.4	,9012
.2	.9008
.12	.9011
.08	.9019
.04	.9033
.02	.9038

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[17] Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).

[18] "International Critical Tables," Vol. VI, 1929, p. 242.

2. From **the** Principle of **Ionic** Strength.—In Set B it was possible to work with solutions whose ionic strength was small enough to enable us to use the equation of Bronsted and La Mer[19] for the activity coefficient of a divalent ion given by the equation

$$-\log \mathbf{f} = 0.5\, z^2\sqrt{\mu} \qquad (4)$$

This Equation 4 does not hold except in solutions whose ionic strength is of the order of 0.01 or less, but since the calculations involving the diameter of the ions, the dielectric constant, the distance of closest approach of the two ions, and others are somewhat uncertain, it was decided to calculate the coefficients by Equation 4 and then to plot the values of E^n (see Table VII), from the equation

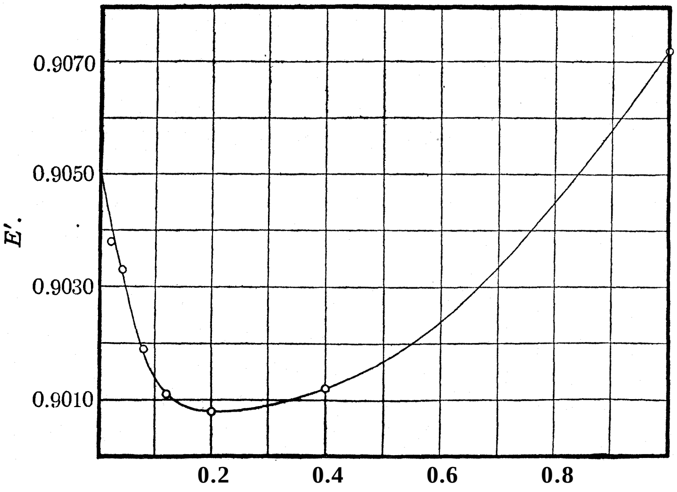

Fig. 3.—The standard oxidation–reduction potential from total concentration.

$$E_{n} = E^{w} - 0.05915/2\left(\log \frac{C_{\mathrm{Hg_2^{++}}}}{C_{\mathrm{Hg^{++}}}^{2}}\right) - 0.05915/2\left(\log \frac{\gamma_{\mathrm{Hg_2^{++}}}}{\gamma_{\mathrm{Hg^{++}}}^{2}}\right) \qquad (5)$$

against the square root of the ionic strength. This plot is given in Fig. 4. On extrapolating the straight line, the value for E_0 was found to be 0.9045.

Table VII

Oxidation–Reduction Potentials from Ionic Strength

μ	f	E"
0.064	**0.312**	**0.9182**
.058	.330	.9177
.052	.350	.9167
.046	,372	.9160
.043	.385	.9155
.026	.476	.9133
.023	.498	.9127

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[19] Brönsted and La Mer, This journal, 46, 555 (1924).

This value was checked mathematically as formerly and was found to be 0.9042.

3. Effect of Acidity and Concentration of Mercury Salts.—When the concentration of the perchloric acid was varied from 0.02 to 1 molal, the oxidation–reduction potential of the mercuric–mercurous electrode went through a minimum at about 0.2 m. Since the effect on the potentials of changing the concentration of the mercury salts (keeping the mercuric equal to the mercurous) from 0.008 to 0.0005 m is practically negligible in each acid series, one may conclude that the liquid junction potentials are negligible. This conclusion seems justified since the potential remains the same even in 0.02 *m* perchloric acid, in which the liquid junction potential should be the largest.

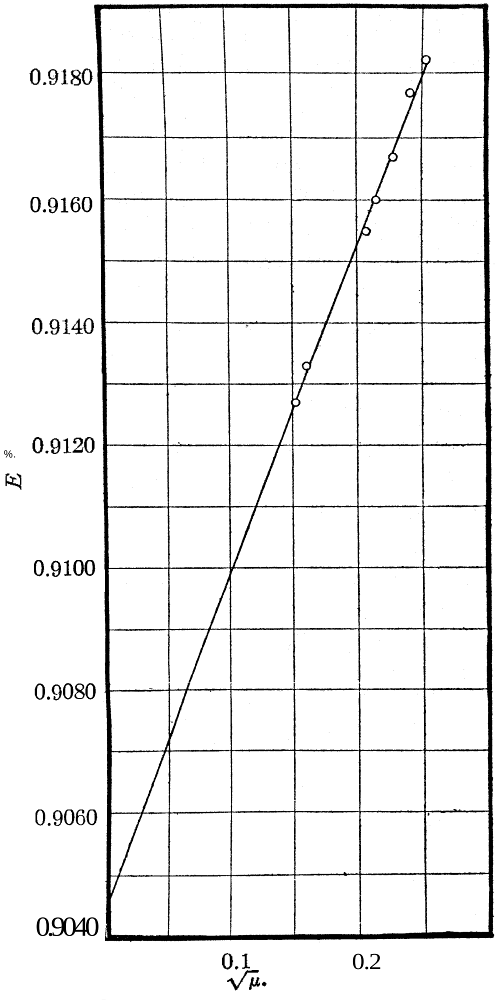

Fig. 4.—The standard oxidation–reduction potential from ionic strength.

4. Comparison with Other Investigations.— The oxidation–reduction potential of the mercuric–mercurous electrode was determined by Carter and Robinson[1] at 18°, using the perchlorates of mercury. They found a value of 0.913 and a much greater variation in the potential with acid concentration. They employed a calomel electrode as the reference electrode, using a potassium nitrate solution as a salt bridge. The use of the bridge in no way eliminates the liquid junction potentials. In all of their calculations they employed the same correction factor, –0.0044 volt, for the activity coefficient regardless of changes in the concentrations of mercury salts. Latimer and Hildebrand[20] give a

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[20] Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," Macmillan Co., New York, 1929, p. 368.

value of -0.92 volt, which was calculated from values given by Abegg, Auerbach and Luther.[21]

5. The Standard Potential.—Since practically the same oxidation–reduction potential for the mercuric–mercurous electrode was obtained from either total concentration or ionic strength, one may justify the final value of 0.9050 volt. For analytical purposes the values in various acid concentrations given in Table VI are of special importance.

Conclusions

1. The standard oxidation–reduction potential of the mercuric–mercurous electrode was determined using the perchlorates of mercury.

2. Using suitable mathematical and graphical treatments as well as the activity coefficients of divalent ions from the limiting case of Bronsted and La Mer's equation, the standard oxidation–reduction potential was found to be 0.9050 v.

3. The mean activity coefficients of perchloric acid solutions were found to be practically of the same order as those for hydrochloric acid solutions up to 0.4 *m*.

4. Methods of analysis involving mercuric and mercurous salts, and acidity in the presence of mercury salts are given.

5. From an analytical standpoint and for all practical purposes, the potentials at various acidities are of greater importance than the standard one and are herein given. The potential goes through a minimum at about 0.2 m perchloric acid.

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[21] Abegg, Auerbach and Luther, "Messungen elektromotorischer Krafte galvanischer Ketten mit wasserigen Elektrolyten," Halle a. S., Verlag v. Knapp, 1911.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES.

IV. THE VALIDITY OF OHM'S LAW FOR ELECTROLYTES[1]

BY GRINNELL JONES AND GILES M. BOLLINGER

RECEIVED OCTOBER 7, 1930 PUBLISHED APRIL 6, 1931

Introduction

Recently M. Wien[2] has published a paper entitled "On a Deviation from Ohm's Law for Electrolytes" in which he has recorded measurements of the conductance of electrolytes in very strong fields from about 30,000 volts per centimeter up to about 300,000 volts per centimeter. He reached the conclusion that a real increase in conductance with increase in field strength occurs at very high voltages. An increase in conductance of more than 50% above the conductance with low voltages was found in one case and smaller increases in many other cases. The feature most clearly established by his experiments is the great influence of the valences of the ions on the Wien effect. He made measurements on twenty-three different salts of varied valence types and concluded that the effect is proportional to the square of the product of the valences of the ions. The effect is greater for concentrated solutions than for dilute. For dilute solutions and for the lower range of voltages for which the effect was measurable he found that the increase in equivalent conductance appears to be proportional to the field strength, but at very high field strengths the conductance appears to approach a definite maximum. He says: "The observation of the limit of the effect as well as its theoretical interpretation is . . . extremely uncertain, and for the present it can only be inferred from the experiments that the limit of the effect agrees at least in rough order of magnitude with the decrease in equivalent conductance from the conductance at infinite dilution. . . . It is probable that the great velocity which the high field imparts to the ions completely or partially abolishes the cause for the change of equivalent conductance with the concentration."

This experimental paper of Wien stimulated the theoretical analysis of the problem by Joos and Blumentritt,[3] based on the interionic attraction

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[1] The earlier papers in this series are: (a) Grinnell Jones and R. C. Josephs, THIS JOURNAL, 50, 1049 (1928); (b) Grinnell Jones and Giles M. Bollinger, *ibid.*, 51, 2407 (1929); (c) 53, 411 (1931).

[2] J. Malsch and M. Wien, *Wied.* Ann. *Physik*, [4] 83, 305 (1927); M. Wien, *ibid.*, [4] 83, 327 (1927).

[3] G. Joos and M. Blumentritt, *Physik. Z.*, 28, 836 (1927); G. Joos, *ibid.*, 29, 755 (1928); M. Blumentritt, Ann. *Physik*, [4] 85, 812 (1928); P. Debye and H. Falkenhagen, *Physik.* Z., 29, 425–426 (1928); M. Blumentritt, Ann. *Physik*, [5] *1*, 195 (1929); H. Falkenhagen and J. W. Williams, *J. Phys. Chem.*, 33, 1124 (1929).

theory of Debye and Hiickel. According to this theory the electric forces between the ions tend to maintain the ions in a space lattice distribution and oppose any displacement of the ions from their position in the lattice by an outside field. Since this braking effect of the interionic electric forces increases with the concentration it accounts for the decrease in mobility of the ions and hence of the equivalent conductance with increasing concentration. But when the solution is subjected to an outside electric field, the resulting motion of the ions tends to destroy the space lattice distribution and give a more random distribution, with the result that the mobility tends to rise until with sufficiently high field strengths it becomes the same as the mobility at infinite dilution.

Joos derived the expression

$$\Delta\Lambda = AX3 - BX^4$$

where M is the increase in equivalent conductance in a field, X (volts/cm.) and A and B are independent of the field strength but vary in a complicated but explicit manner with the temperature, and with the dielectric constant and viscosity of the solution, and with the valences, mobilities and concentrations of all of the ions.

These theoretical papers in turn stimulated Wien[4] to a renewed experimental study of the problem with an improved technique which permitted the effect to be measured with field strengths as low as 3000 volts per centimeter. Although the precision attained in these difficult experiments is not great, they appear to support the theoretical deductions of Joos.

If, as seems probable, Wien's experiments are reliable, it means that Ohm's Law is not strictly valid for electrolytes over the entire range of voltages.[5] The Wien effect must therefore be of interest and importance in the theory of solutions but it is not necessarily significant for the measurement of conductance by the Kohlrausch method, because the field strengths used by Wien were at least 1000 to 100,000 times as great as those commonly used in the Kohlrausch method. It may be inferred from Wien's data that the effect will be entirely negligible in the weak fields suitable for the Kohlrausch method. This is encouraging but not entirely conclusive because the form of the function as given by Joos is not well established nor can the value of the coefficients be precisely determined from Wien's experiments. A direct experimental test at low voltages is

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[4] M. Wien, *Ann. Physik,* [4] 85, 795 (1928); [5] 1, 400 (1929).

[5] Incidentally it is of interest to point out that P. W. Bridgeman [*Proc. Am. Acad.,* 57, 131 (1922)] has made experiments on the electric conduction of thin strips of gold and of silver at high current densities which he interprets as showing that Ohm's Law is not strictly valid for metallic conductors. "The maximum current densities were about 5×10^6 amp./cm.^{2}, and the deviations from Ohm's Law were of the order of one per cent." This interpretation of these experiments has, however, been challenged by H. M. Barlow, *Phil. Mag.,* [7] 9, 1053 (1930).

therefore desirable—especially since there are also reports in the literature of an apparent variation in the resistance of electrolytes with variation of applied voltage as determined by the Kohlrausch method.

Comparatively few of the earlier experimenters on the conductances of electrolytes by the Kohlrausch method have purposely varied the voltage which they used and observed the effect, if any, on the apparent resistance. An apparent change of resistance with voltage (or with the current density, which amounts to the same thing) and which may be ascribed to polarization, has been observed by several experimenters, including Wien, Haworth, and Percy;[6] but experiments in which the disturbing effect of polarization are avoided are more pertinent for our present purpose.

Early in his work on conductance, Kohlrausch,[7] having first devised a technique which minimized polarization, tested the validity of Ohm's Law for electrolytes and found no variation of resistance with the voltage applied to the bridge greater than the errors in his measurements, although the precision attained in this early work was much below more modern standards.

More recently several experimenters have found a change in apparent resistance with change in voltage even when using conditions favorable for the elimination of polarization.

Taylor and Acree[8] report variations in apparent resistance as large as 0.08% in unclean cells when the voltage was changed from 0.25 to 2 volts, but they state that no such effect was observed with clean cells.

Kraus and Parker[9] do not accept the suggestion that lack of cleanliness is the sole reason for a variation in resistance with the voltage applied. They report that in their experiments a change in voltage from 0.2 to 7.0 volts caused a decrease of 0.02% in the apparent resistance when using iodic acid solutions and an increase of about the same magnitude with potassium chloride solutions. "It was not found possible to locate the cause of this effect in the limited time available. . . ."

This question has been further studied by Parker,[10] who gives a curve showing the apparent percentage increase in resistance caused by varying the voltage applied to the bridge from 0.2 volt to 10 volts with numerous different solutions of potassium chloride covering the range from very low resistances up to nearly 10,000 ohms. He found that the higher voltage gave the higher resistance throughout the range so that the effect cannot be ascribed to heating. At low resistances variations up to 0.13% were

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[6] M. Wien, *Wied. Ann. Physik*, 58, 44 (1896); H. F. Haworth, *Trans. Faraday Soc.*, 16, 370 (1921); R. H. Percy, "Dissertation," Basel, 1922.

[7] F. Kohlrausch and W. A. Nippolt, *Pogg. Ann.*, 138, 280-298, 370-390 (1869); see especially pp. 370 and 378; F. Kohlrausch, *Wied. Ann.*, 6, 9 (1879); 26, 168 (1885).

[8] W. A. Taylor and S. F. Acree, THIS JOURNAL, 38, 2416 (1916).

[9] C. A. Kraus and H. C. Parker, *ibid.*, 44, 2438 (1922).

[10] H. C. Parker, *ibid.*, 45, 1370 (1923).

shown. Within the range from 1000 to 6000 ohms, the difference was about 0.02% and rose to nearly 0.04% at about 10,000 ohms. Parker concluded that there are two different causes for the variation, superimposed on each other. He ascribes the controlling influence at low resistances to polarization. With increasing resistance the polarization dwindles and yet the influence of change in voltage on the resistance passes through a minimum and then rises. This clearly indicates that there is some effect other than polarization influencing the results. Parker does not express an opinion as to the nature of the effect.which predominates at the higher resistances, nor as to whether the results obtained with the high or the low voltage are more nearly correct. Morgan and Lammert, after referring to the papers of Taylor and Acree and of Kraus and Parker cited above, say: "In the present research no change in resistance with the change in impressed voltage has been observed when the electrodes were properly cleaned." The range used is not stated.[11]

Experimental Part

Since we had available a new and improved bridge,' it became of interest to determine whether or not the deviations from Ohm's Law detected by Wien are detectable at voltages suitable for use in the Kohlrausch method and to endeavor to decide whether the apparent failure of Ohm's Law reported by Taylor and Acree, Kraus and Parker, and Parker is real or due to experimental error. With very low resistance (under 100 ohms) and a high voltage (4 volts or more) we have observed small changes in apparent resistance with change in voltage, but under these conditions the heating effect of the current on the cell is sufficient to make precise measurements difficult and polarization occurs, so that the apparent changes in resistance are not believed to be significant. In some of our earlier work, small voltage effects were detected which could not be ascribed to polarization or to heating and were traced to mutual inductance between the oscillator and the bridge[1b] and the detector. It was shown that the results with the higher voltage were more nearly correct since the effect of mutual inductance had a relatively greater influence when the voltage impressed on the bridge was low. After the oscillator was moved to a safe distance, the influence of variation in voltage applied on the measured resistance disappeared entirely when measuring 300 ohms or more as is demonstrated by the data in Table I.

The cells designated by A, D and G are of the pipet type. Cells K, L, M and N are of our new type designed to minimize the effects of capacitance between parts of the cell and have been described and illustrated in the third paper of this series.[1c] Cell Z is also of the new type. It has a capillary tube 70 cm. long and with a bore of about 0.9 mm., giving an

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[11] J. L. R. Morgan and O. M. Lammert, THIS JOURNAL, 45,1704 (1923).

TABLE I

EXPERIMENTAL RESULTS

Cell	Separation of electrode, cm	Cell constant	Frequency, cycles per second	Spec. cond. of soln. used	Volts across bridge	Field strength, volts/cm.	Resistance, ohms
K	1.5	0.67	1090	0.0022	4.2	1.4	299.11
					0.01	0.003	299.11
M	11.5	11.7	1090	.011	4.2	.18	1,105.67
					0.4	.017	1,105.70
					.01	.0004	1,105.70
G	5	3.06	500	.0017	2.3	.23	1,770.25
					0.1	.01	1,770.28
D	12	12.38	2280	.0050	5.26	.22	2,468.96
					0.8	.03	2,468.97
N	16.5	126.7	3000	.022	5.0	.15	5,638.9
					1.0	.03	5,638.8
					0.1	.003	5,638.9
L	6	2.63	1090	.00021	4.2	.35	12,395.0
					0.6	.05	12,395 0
					0.01	.0008	12,395.0
Z	70	10600	1090	.51	4.2	.03	20,487.72
					.05	.0004	20,487.7
					0.02	.00014	20,488
N	16.5	126.7	3000	.0042	5.0	.15	29,712.5
					0.1	.03	29,712
N	16.5	126.7	4000	.0023	5.0	.15	55,307
					0.5	.015	55,306
A	16	144.6	1090	.0026	4.2	.13	56,097
					9.6	.02	56,098

exceptionally high cell constant. With some of these cells an appreciable variation of apparent resistance with frequency may be observed, whereas others are free from this fault The electrolyte used was potassium chloride in all cases except the experiments with cell Z, which was filled with a solution of sulfuric acid having approximately the maximum specific conductance. The variations in measured resistance shown in the table might all be caused by a variation of 0.001°C. in the temperature and are regarded as insignificant. These data, selected from many others of like import in our notebooks, show that when suitable experimental precautions are taken to avoid heating and polarization, and when using a bridge properly designed to avoid complications inherent in working with alternating current, the voltage used is without effect on the measured resistance, over a wide range of frequencies and of resistances and with cells of widely varying design, throughout the range of voltages which are useful for the practical measurement of the conductance of electrolytes by the Kohlrausch method.

Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for the expenses of this investigation.

Summary

Wien has shown experimentally that deviations from Ohm's Law amounting to more than 50% in some cases occur in electrolytes at very high field strengths (3000 to 300,000 volts per centimeter). It is demonstrated in this paper that if adequate experimental precautions are taken to avoid errors due to heating, to polarization, and to the secondary effects of inductance and capacitance, there is no measurable variation of the real resistance of electrolytes with variation of the applied voltage throughout the range of voltages and frequencies suitable for use in the Kohlrausch method of measuring electrolytic conductance. Ohm's law may, therefore, be regarded as valid for electrolytes under these conditions.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES AND THE KENT CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

THE STRUCTURE OF FERRIC THIOCYANATE AND THE THIOCYANATE TEST FOR IRON

BY H. I. SCHLESINGER AND H. B. VAN VALKENBURGH[1]

RECEIVED DECEMBER 15, 1930 PUBLISHED APRIL 6, 1931

The usual explanation of the thiocyanate test for ferric ions assumes that the red color is due to the formation of un-ionized ferric thiocyanate, but there is no convincing evidence that dilute aqueous solutions of ferric thiocyanate are only very slightly ionized. Even if they were, it seems unlikely that the union of slightly colored ferric ion with colorless thiocyanate ion should produce a highly colored molecule, since simple ionic dissociation is usually not accompanied by marked color changes. On the other hand, it has been known for a long time that the action of an excess of ammonium or alkali thiocyanate on ferric salts leads to the formation of highly colored substances of the type $Me_3[Fe(CNS)_6]$.[2] That the formation of the complex ion $[Fe(CNS)_6]^{\equiv}$ has not been generally accepted as an explanation of the reaction is due to two causes. In the first place, the solid salts do not appear to have a color exactly identical with that of the solutions in question. In the second place, these salts are not soluble in dry ether, which, as is well known, extracts the colored substance from

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[1] This article is taken from a thesis presented by H. B. Van Valkenburgh to the Ogden Graduate School of Sciences in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Krüss and Moraht, *Ann.*, 260, 193 (1890); Rosenheim and Cohn, *Z. anorg. Chem.*, 27, 280 (1901).

aqueous solutions. The ethereal solutions thus obtained do not contain either ammonium or alkali salts.

Both of these objections to the hypothesis that the color of the solutions is due to the complex ferric thiocyanate ion $[Fe(CNS)_6]^{\equiv}$ can be easily met. Solid salts frequently exhibit shades of color which differ from those of their solutions. Furthermore, the absorption spectra[3] of aqueous solutions of salts of the type $Me_3Fe(CNS)_6$ of ethereal extracts of these solutions, of aqueous solutions of ferric thiocyanate and of solutions of anhydrous ferric thiocyanate in anhydrous ether exhibit practically identical absorption spectra,[4] as shown in Figs. 1 and 2. These facts indicate that the light-absorbing substances are the same in these three types of solutions, and

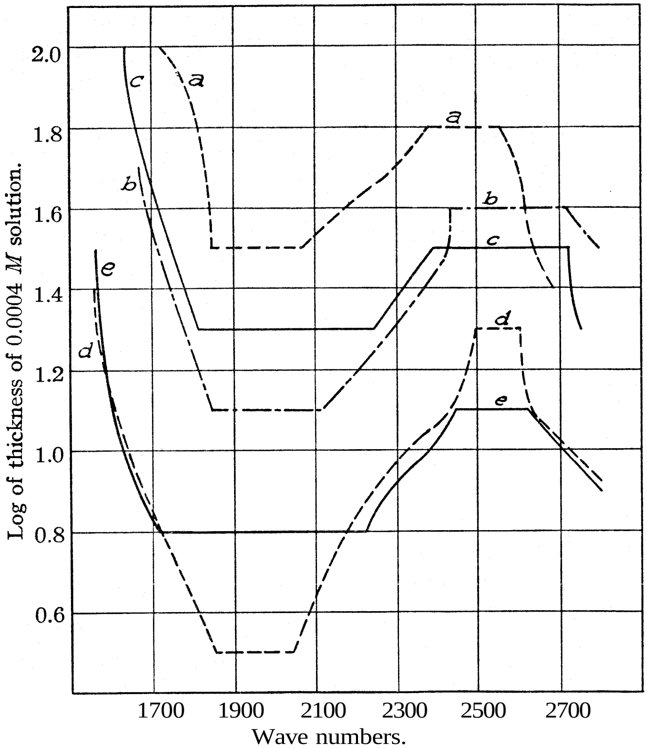

Fig. 1.—Absorption spectrum of $Fe(CNS)_3$: a, 0.0004 *M*, c, 0.0008 *M*, in water; d, 0.0002 *M*, e, 0.0004 *M*, in ether; of $Na_3Fe(CNS)_6$: b, 0.0004 *M* in wafer.

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[3] The absorption spectra were photographed with a Hilger quartz spectrograph. A description of the apparatus and experimental procedure will be found in an article by Schlesinger and Salathe, This journal, 45, 1871 (1923).

[4] The slight differences in the absorption spectra are due to the addition of thiocyanic acid to the aqueous solutions of ferric thiocyanate to prevent hydrolysis, and to unavoidable differences in the unknown concentration of the actual absorbing substance.

therefore exclude the possibility that the red color is due, as might be otherwise imagined, to an ether-soluble, non-ionizable aquo compound, $\left[Fe^{(CNS)_3}_{(H_2O)_3}\right]$. The latter conclusion is corroborated by the finding that electrolysis of aqueous solutions of ferric thiocyanate causes the red color to migrate toward the anode, while ferric ions pass toward the cathode.

The identity of the absorption spectra of solutions of hexathiocyanate salts and of ferric thiocyanate, as well as the ionic migration experiment, suggest that solutions of the supposedly simple salt also contain the complex ion. If that is the case the formula $Fe[Fe(CNS)_6]$ should be assigned to ferric thiocyanate. That this assumption is correct is borne out by the fact that in anhydrous ethereal solutions, as well as in benzene, its molecular weight is practically twice that corresponding to the simple salt. In aqueous solutions, unless a large excess of thiocyanate ion is present, the complex ion is more or less dissociated; thus are explained the slight differences in absorption spectra noted above.[4] Furthermore, if a large excess of thiocyanate ions is added to the aqueous solutions, all of the ferric ion is converted into the complex ion and ether can no longer extract $Fe[Fe(CNS)_6]$ from the solutions. These conclusions are in agreement with the facts.

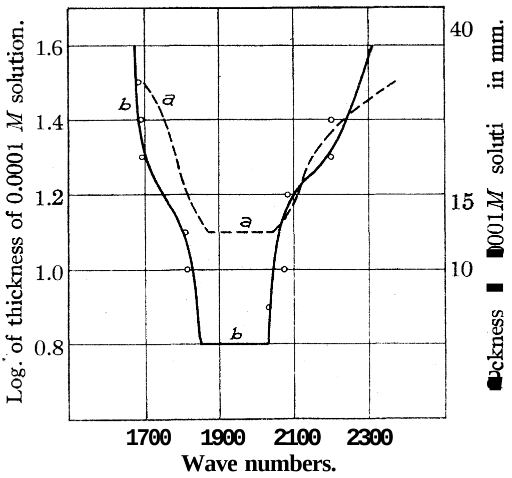

Fig. 2.—Absorption spectra of ethereal extracts: a, 0.0004 M $Na_3Fe(CNS)_6$; b, 0.0001 M $(NH_4)_3Fe(CNS)_6$.

Only one point remains to be discussed. The effect of ammonium chloride in decreasing the color of ferric thiocyanate solutions was formerly explained as being due to the reaction: $3NH_4Cl + Fe(CNS)_6 \rightleftharpoons 3NH_4CNS + FeCl_3$. A more logical explanation is the reaction represented by the equation: $[Fe(CNS)_6]^{\equiv} + 6Cl^- \quad [FeCl_6]^{\equiv} + 6CNS^-$. The existence of a hexachloroferric ion is not unwarranted in view of the well-established existence of the corresponding fluoro ferric ion; furthermore, addition of chloride ions to ferric salt solutions alters the absorption spectra of the latter, indicating complex ion formation, as is described below.

Experimental

Preparation of Ferric Thiocyanate.—**The preparation of anhydrous ferric thiocyanate proved very troublesome until it was discovered that the products of decompo-**

sition of the substance in solution could be excluded from the crystals only if crystallization was carried out very slowly. Equivalent quantities of solutions of barium thiocyanate and ferric sulfate were mixed, and the solution, after standing for some time, was filtered to remove barium sulfate, and placed over sulfuric acid in a brown desiccator until a small crop of crystals had formed. The crystals were removed by decantation of the solution, which was again allowed to evaporate. This process was repeated several times until crystals of constant composition were obtained. Various samples of such material gave an iron content of 24.49 ± 0.02%; calculated for $Fe(CNS)_3$, 24.29%.

Preparation of Sodium Ferric **Hexathiocyanate.**—This salt was obtained according to the directions of Rosenheim and Cohn.[2] It was found that the compound $Na_3Fe(CNS)_6 \cdot 12H_2O$, described by them, loses water over sulfuric acid, yielding a trihydrate.

The absorption spectra of the various thiocyanates in aqueous and ethereal solutions have already been adequately described. Figure 3 shows the effect of the addition of ammonium chloride to 0.02 and 0.002 *M* solutions of ferric chloride, acidified with a small amount of hydrochloric acid to prevent hydrolysis. It is seen that the addition of the chloride shifts the end absorption markedly toward the longer wave lengths.[5] Such changes indicate the formation of a new compound, presumably a complex ion.

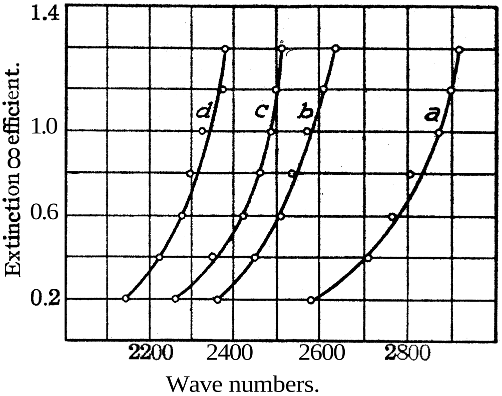

Fig. 3.—Absorption spectrum of aqueous solutions of $FeCl_3$: a, 0.002 *M;* b, 0.002 *M* $FeCl_3$ + 2.0 *M* NH_4Cl; c, 0.02 *M;* d, 0.02 *M* $FeCl_3$ + 1.0 M NH_4Cl.

Determinations of the molecular weight of ferric thiocyanate in benzene were made by the freezing point method and in ether by the boiling point method. The apparatus of Menzies, as well as that of Washburn–Cottrell, was used in the latter. The benzene was carefully distilled twice and showed a constant freezing point. The ether was purified in the usual manner and finally distilled twice from sodium. It had a constant boiling point. The results of the molecular weight determinations are shown in Table I. Both in benzene and in ethereal solutions ferric thiocyanate undergoes moderately rapid spontaneous decomposition as already described by Rosenheim and Cohn.[2] Among the products of decomposition are polymerized derivatives of thiocyanic acid. It is therefore not surprising that the results are on the whole somewhat higher than values corresponding to twice the molecular weight of $Fe(CNS)_3$. The agreement of individual values is as good as is to be expected in view of the instability of the solutions.

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[5] The measurements were made with the Hilger spectrograph and sector photometer.

TABLE I

MOLECULAR WEIGHT OF FERRIC THIOCYANATE

In ether

Subs., g.	Soln., cc.	Elevation of b. p., °C.	Molecular weight Found	Molecular weight Calcd. for $Fe[Fe(CNS)_6]$
0.3400	32.2	0.0730	483	460
.1806	32.0	.0411	458	
.2045	32.1	.0452	471	
	Ether, g.			
.1770	**70.443**	.011	**482**	
		Average	**473**	

In benzene

Subs., g.	Benzene, g.	Lowering of f. p., °C.	Molecular weight Found	Molecular weight Calcd. for $Fe[Fe(CNS)_6]$
0.021	**24.397**	**0.010**	**448**	**460**
.027	**23.658**	.012	**495**	
.018	**20.153**	.010	**465**	
		Average	**469**	

This research is one of a series of investigations carried out with the aid of a grant from the Bache Fund of the National Academy of Sciences.

Summary

1. In aqueous solutions of ferric thiocyanate the red color migrates to the anode during electrolysis.

2. The red color of these solutions is shown by their absorption spectra to be identical with that of aqueous solutions of salts containing the complex ion $[Fe(CNS)_6]^{\equiv}$ and with ethereal solutions of anhydrous ferric thiocyanate.

3. In the latter as well as in benzene, ferric thiocyanate has a molecular weight approximately twice that corresponding to the formula of the simple salt. On the basis of these results it is concluded that the red color observed in the thiocyanate test for iron is due to the ion $[Fe(CNS)_6]^{\equiv}$, and that ether extracts the compound $Fe[Fe(CNS)_6]$, from aqueous solutions. The diminution in color caused by ammonium chloride is ascribed to the formation of a hexachloro ferric ion.

CHICAGO, ILLINOIS

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

THE SOLUBILITIES OF LANTHANUM OXALATE AND OF LANTHANUM HYDROXIDE IN WATER. THE MOBILITY OF THE LANTHANUM ION AT 25°

BY I. M. KOLTHOFF AND RUTH ELMQUIST[1]

RECEIVED DECEMBER 22, 1930 PUBLISHED APRIL 6, 1931

In a study of the quantitative determination of lanthanum by precipitation as lanthanum oxalate and as hydrous lanthanum oxide—the results of which will be discussed in a later paper—it was of interest to know the solubilities of the two slightly soluble compounds in water. Since the saturation values are extremely small, the electrical conductance method can be applied advantageously. As will be shown later, the results of the latter method have to be accepted with caution and, therefore, the data have been verified by volumetric and sometimes by colorimetric procedures.

Materials Used.—The lanthanum compounds were prepared from lanthanum ammonium nitrate procured through the courtesy of Dr. H. S. Miner of the Welsbach Company, Gloucester, New Jersey. The arc spectrum of this material photographed with a quartz spectrograph showed entire freedom from any other rare earth elements. It was treated with ammonium hydroxide and hydrogen peroxide to insure absence of any cerium, using sufficient excess of ammonia to precipitate a small amount of lanthanum with any cerium that might be present. Following this, the lanthanum was precipitated with oxalic acid a number of times with thorough washing each time. The air-dry oxalate was converted into the oxide by ignition in an electric furnace at 800° to constant weight. An excess of this oxide was added to hydrochloric acid which had been prepared by bubbling hydrogen chloride into redistilled water. After the excess had been filtered off, the lanthanum chloride was crystallized from the solution and then twice recrystallized from conductivity water. The crystals containing seven molecules of water were kept in a desiccator over deliquescent calcium chloride. Lanthanum and chloride were determined quantitatively; the results agreed within 0.1%. The PH of the 0.1 molar solution, determined colorimetrically with adjusted brom thymol blue as an indicator in carbon dioxide-free water as a solvent was 6.2.[2]

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[1] From a thesis submitted by Ruth Elmquist to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] The data reported by J. H. Kleinheksel and H. C. Kremers [THIS JOURNAL, 50, 959 (1928)] are not in agreement with our results. Their figures on the hydrolysis of salts of rare earth elements cannot be accepted as being reliable since they prepared the anhydrous salts in a stream of hydrochloric acid and did not give any proof that no free acid was adsorbed or occluded by the crystals. From their experimental figures (p. 965) it is quite evident that the acidity of lanthanum chloride reported was due to the presence of free hydrochloric acid.

Lanthanum **Oxalate.**—This was prepared by precipitating a solution of pure lanthanum chloride with pure oxalic acid. The precipitated lanthanum oxalate was washed with distilled water until the P_H of the wash water remained unchanged (methyl red as indicator) and then repeatedly washed with conductivity water. The air-dried crystals contained ten molecules of water.

Lanthanum Oxide and Hydrous Lanthanum Oxide.—Three samples of lanthanum oxide were used, one prepared from lanthanum hydroxide, the second from lanthanum oxalate and the third from lanthanum nitrate. All three had been ignited to constant weight in an electric furnace at 800°. Also freshly precipitated hydrous lanthanum oxide was used. It was prepared by slowly adding a solution of pure lanthanum chloride to an excess of ammonium hydroxide. An attempt was made to wash the hydrous oxide free from electrolytes in the filtering apparatus of Bachmeyer and thus protect it from carbon dioxide of the air. On account of the gelatinous character of the precipitate this purification method had to be given up. Good results were obtained by centrifuging the precipitate several times with carbon dioxide-free water until the conductance of the saturated solution remained unchanged upon further washing. The wet precipitate was quickly transferred to the conductance cell. The various oxides and the hydrous oxide absorb carbon dioxide from the air very readily; the order of the solubility is changed entirely even by traces of this impurity.

Conductivity Water.—Conductivity water was distilled over sulfuric acid, then over barium hydroxide and finally without any addition to remove traces of acid and alkaline impurities. It was collected in aged Pyrex flasks with precautions against contamination from the air. In equilibrium with the air it had a conductivity of 0.80 to 0.85 × 10^{-6} rec. ohms. It could be kept for a week in the Pyrex flasks without change in conductance.

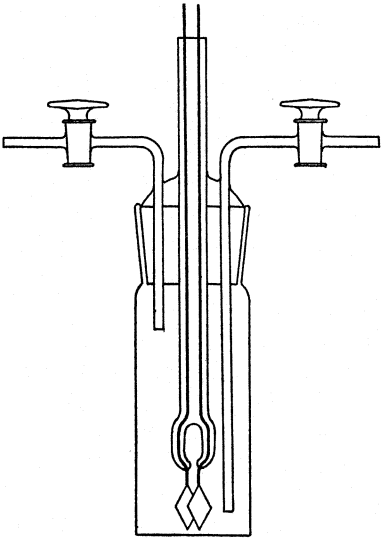

Fig. 1.

Arrangement for the Measurement of the Conductance.—A Leeds and Northrup Wheatstone bridge (rheostat with ratio arms, accuracy 0.1%) was used in this work. Although a condenser was used to balance most of the interference by capacitance, some error was introduced by the latter and by induction. These errors, however, are small compared with other experimental errors in measuring extremely dilute electrolyte solutions.

Conductivity cells of the Washburn type were used for the measurement of solutions with a concentration greater than 0.001. Special cells were constructed for the measurement of the conductance of extremely dilute solutions. The type of cell is given in Fig. 1. The platinum electrodes, which had a diameter of about 25 mm., were placed at a small distance from each other, making the constants of all the cells of the order of 0.01. The electrodes were kept in position by four glass beads at the corner.

Air could be passed through the cell to make the water or solution carbon dioxide free or to put it in equilibrium with the normal air. When equilibrium water was prepared the air from the air pressure in the laboratory was bubbled through a train of two wash bottles containing dilute permanganate, two bottles containing 0.01 *N* sulfuric acid and three with pure water, the last one being mounted in the thermostat. A similar arrangement was used when the water had to be made carbon dioxide free, but three large towers filled with soda lime were then placed between the permanganate and sulfuric acid bottles and a fourth tower after the last flask in the thermostat, The thermostat was kept at 25 ± 0.05°.

For solutions with a concentration smaller than 0.0001 *N*, bright platinum electrodes have to be used, with slightly platinized electrodes irregularities and deviations of the order of 1% are observed. The effect is much smaller than L. de Broeckère[3] noted. With dilute hydrochloric acid solutions the effect is slightly greater than with neutral salts. When using even slightly platinized electrodes, dilute alkaline solutions cannot be measured with any degree of accuracy on account of the relatively strong adsorbent power of the platinum black.[4] In working with extremely dilute alkaline solutions the Pyrex vessels must be paraffined or coated with some other inert material to prevent the attack of the glass by alkali. After the coat has been thoroughly cleaned, constant and reproducible results are obtained even with sodium hydroxide solutions more dilute than 0.0001 N. Some measurements were made in the following way. A measured volume of water (about 200 cc.) was placed in the cell and made carbon dioxide free by passing through purified air. A 0.01 *N* sodium hydroxide solution was added from a microburet with the air still bubbling through. The inlet and outlet tubes were closed by the glass stopcocks and the readings made. After subtracting the conductivity of the carbon dioxide-free water (0.12×10^{-6} rec. ohms) an equivalent conductance of 250 was found for 0.0001 N sodium hydroxide and of 249.2 for 0.00005 N base at 25°.

In determining the conductivity of a saturated solution of lanthanum hydroxide, the water was made carbon dioxide free and the pure oxide or hydrous oxide was added quickly with the air still bubbling through. Readings were taken until the resistance was constant.

The Water Correction.—An excellent review on the "water correction"

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[3] L. de Broeckère, *J. chim. phys.*, **25**, 294 (1928).

[4] *Cf.*, *e.* g., Wi. Ostwald, *J. prakt. Chem.*, 33, 352 (1886); 35, 112 (1887); Bredig, *Z. physik. Chem.*, 13, 289 (1894); Jones, *Am. Chem. J.*, **26**, 428 (1901); Bousfield and Lowry, *Phil. Trans.*, **204**, 292 (1905); A. A. Noyes, *Publ. Carnegie Inst.*, 262 (1907); Frary and Nietz, THIS JOURNAL, 37, 2263 (1915); Raikes, Yorke and Ewart, *J. Chem. Soc.*, 128, 635 (1926); Ferguson and Vogel, *Phil. Mag.*, [7] 4, 300 (1927); M. Randall and C. C. Scalione, THIS JOURNAL, **49**, 1486 (1927).

has been written by J. Kendall.[5] He prefers to work with pure water which is a saturated solution of carbon dioxide under atmospheric conditions (equilibrium water). E. W. Washburn[6] showed, however, that it is impracticable to extend conductivity measurements in equilibrium water as long as the slightest uncertainty exists as to the exact purity of the water to such high dilutions. Therefore, he worked under those conditions with ultra pure water having a conductivity of 0.06 X 10^{-6} rec. ohms at 18°. From Kendall's work different authors[7] improperly concluded that carbon dioxide is the only contaminant of good conductivity water, and that the carbonic acid content can be computed from the conductance by means of Kendall's table. Hence they use this water even if not in equilibrium with the air. There are various objections to such a procedure. Even if the equilibrium water at 25° has a conductance of 0.8 X 10^{-6} rec. ohms (which is the theoretical value if carbon dioxide is the only impurity of electrolytic nature), there is no guarantee that carbon dioxide is the only contamination. In our experiments equilibrium water with a conductance of 0.80 to 0.85 X 10^{-6} at 25° had a residual conductance of 0.11 to 0.14 X 10^{-6} after removing all the carbon dioxide. In working with extremely dilute solutions of neutral salts there is no objection to the use of equilibrium water if the water is brought *into equilibrium with air at the temperature at which the measurements are made.* This point is often overlooked, and if the above condition is not fulfilled the water correction will become uncertain, for the conductance of the water will change when exposed to the air. As an illustration some values of the cell constant determined with extremely dilute solutions of potassium chloride in equilibrium water (conductance 0.85 × 10^{-6}) and in the same water when carbon dioxide free (cond. 0.12 × 10^{-6}) will be given. The conductance of the water is subtracted as a correction. The agreement is satisfactory.

Concentration of KC1	Cell constant using equilibrium water	Cell constant using carbon dioxide-free water
0.0005 N	0.01242	0.01240
.00025 N	.01240	.01239
.0001 *N*	.01241	,01239
.00005 N	.01238	.01241

In the measurements of the conductance of extremely dilute lanthanum chloride solutions and in the determination of the solubility of lanthanum oxalate, both equilibrium water and the latter freed from carbon dioxide have been used. The conductivity of the water was subtracted as a correction and the results of both sets of measurements as a rule agree to

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[5] J. Kendall, THIS JOURNAL, 38,2460 (1916); **39,** 7 (1917); see also, I. M. Kolthoff, *Rec. trav. chim., 48,* 664 (1929).

[6] E. W. Washburn, THIS JOURNAL, 40, 106 (1918).

[7] H. Remy, *Z. Elektrochem.,* **31,** 88 (1925); Remy and Kuhlmann, Z. *anal. Chem.,* **65, 1 (1924);** *E.* **Laue,** *Z. anorg. allgem. Chem., 165,* 305 (1927).

within 0.3%. In order to get reliable results from the conductance measurements of a saturated solution of the slightly soluble lanthanum hydroxide, carbon dioxide-free water has to be used as a solvent. Its conductivity was subtracted from the figure, which may cause a slight uncertainty in the result.

The Conductance of Lanthanum Chloride Solutions and the Mobility of the Lanthanum Ion.—The conductance of lanthanum chloride solutions was measured at different dilutions in various cells. The duplicates agreed within 0.1%.

Conductance of Lanthanum Chloride at 25°.—**Conductivity** of equilibrium water, 0.8×10^{-6}; of carbon dioxide-free water, 0.15×10^{-6} rec. ohms. These figures have been subtracted from the conductances of the solution.

Normality of $LaCl_3$	Cond. $\times 10^6$ in equilibrium water	Cond. $\times 10^6$ carbon dioxide-free water	Normality of $LaCl_3$	Cond. $\times 10^6$ in equilibrium water	Cond. $\times 10^6$ carbon dioxide-free water
0.0100	1220	...	0.000599	84.75	84.66
.0050	639	...	.000435	62.17	61.97
.0025	331.7	...	.000261	37.74	37.65
.001501	204.2	203.8	.000150	22.02	22.00
.0010	138.2	138.2	.000075	11.13	11.07
.000745	104.3	104.4	.000060	8.97	8.43

The empirical equation of Kohlrausch[8] in which A is the equivalent

$$\Lambda = \Lambda_\infty - A\sqrt{c}$$

conductivity at a normality c, and A, the same at infinitely dilute solution, is theoretically the limiting expression to which the data will approach

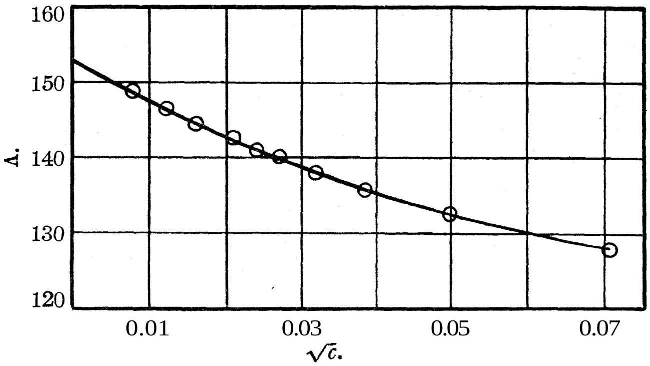

Fig. 2.

more and more closely as the concentration approaches **zero.**[9] In Fig. 2 the equivalent conductance is plotted against the square root of the

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[8] F. E. **Kohlrausch and M. E.** Maltby, *Wiss. Abh. Physik.-Techn.*, **Reichsanstalt, 3,** 156 (1900).

[9] L. **Onsager,** *Physik. Z.*, **27, 388 (1926); 28,277 (1927);** *Trans. Faraday Soc.*, **23, 341 (1927).**

normality c; the line is straight at concentrations smaller than 0.0008 N. From the graph it can be seen that up to concentrations of 0.0008 to 0.001 *N* the following relation holds for lanthanum chloride

$$\Lambda = 152.8 - 475\sqrt{c}$$

The following table shows the calculated and experimental data of the equivalent conductance up to a normality of 0.001 N.

EQUIVALENT CONDUCTANCE OF LANTHANUM CHLORIDE

$\Lambda_{\text{calcd.}} = 152.8 - 475\sqrt{c}$

Normality of $LaCl_3$	$\Lambda_{\text{exptl.}}$	$\Lambda_{\text{calcd.}}$	Difference in %
0.001	138.2	137.8	+0.3
.000745	140.0	140.0	0.0
.000599	141.3	141.3	0.0
.000435	142.6	143.0	−0.3
.000261	144.7	145.3	−0.4
.000150	146.6	147.1	−0.3
.000075	148.8	148.8	0.0
.000060	149.4	149.2	+0.1

At concentrations between 0.001 and 0.01 N the following relation holds

$$\Lambda = 152.8 - 146\sqrt[3]{c}$$

Using the value 75.8 for the mobility of the chloride ion at infinite dilution[10] a value of 77 is found for the equivalent conductance of the lanthanum ion at an ionic strength of zero. This value is higher than those reported in the literature. H. Ley[11] found 67.3, A. A. Noyes and J. Johnston[12] 72.0, and Rimbach and Schubert,[13] 67.3. The measurements described in this paper have been extended to extremely high dilutions and the extrapolated figure of Λ, therefore is more certain than that of previous authors.

The Solubility of Lanthanum Oxalate in Water at 25°

(a) Conductivity Method.—The conductance of a saturated solution of lanthanum oxalate (three different products) in equilibrium water and carbon dioxide-free water was determined at 25°. After subtracting the conductivity of the solvent, a specific conductance of $9.97\ (\pm 0.1) \times 10^{-6}$ rec ohms was found. Assuming complete ionization and a value of 77 for the mobility of the lanthanum ion and of 72.7 of the oxalate ion,[14] this conductance corresponds to a solubility of 0.60 mg. of the anhydrous salt per liter or a molarity of 3.35×10^{-6}.

(b) Volumetric Method.—Saturated solutions of three different products of lanthanum oxalate were prepared in conductivity water by shaking an excess of the solid with 2.5 liters of water for a week in a thermostat at 25 ± 0.05°. After settling in the thermostat, large samples were removed by means of a pressure pipet and each sample examined in a strong light to make sure of the absence of any suspended solid. Two

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[10] F. L. Hunt, THIS JOURNAL, **33,** 795 (1911).

[11] H. Ley, *Z. physik. Chem.,* **30,** 193 (1899).

[12] A. A. Noyes and J. Johnston, THIS JOURNAL. **31,** 987 (1909).

[13] Rimbach and Schubert, *Z. physik. Chem.,* **67,** 183 (1909).

[14] F. Kohlrausch and Holborn, "Leitvermogen der Elektrolyte," **1916.**

liters were evaporated to a small volume (about 25 cc.) and the oxalate titrated with 0.01 *N* permanganate. A solubility of 2 0X ± 0.03 mg. of anhydrous oxalate per liter was found in this way.

(c) Colorimetric Method.—As there was a large discrepancy between the conductimetric and volumetric methods, the solubility was approximated in a colorimetric way. It was found that a dilute solution of sodium alizarinate gives a bright violet color to a solution of lanthanum containing as little as 1 mg. of the latter in a liter. This test can be applied successfully to the colorimetric estimation of lanthanum in extremely small concentrations down to 0.1 mg. of lanthanum per liter. At a definite lanthanum content the sensitivity and the color observed are dependent upon the hydrogen-ion concentration. In order to get comparable conditions, 1 cc. of an acetate buffer containing *2 N* ammonium acetate and *2 N* acetic acid is added to 10 cc. of the nearly neutral solution to be tested. Then 0.4 cc. of a 0.1% sodium alizarinate solution is added and comparison made with lanthanum solutions of known content. The method gives good results for concentrations between 0.1 and 2 mg. of lanthanum per liter. The solutions for comparison cannot be kept for a long time as the lanthanum alizarinate compound flocculates as a purple precipitate after standing for ten to twenty hours. Oxalate interferes somewhat with this color test; therefore, in the determination of the solubility of lanthanum oxalate the anion was replaced by sulfate. Five, 10 and 20 cc. samples of the saturated solution were evaporated to dryness. A little sulfuric acid was added to the residue, which was then heated until no more fumes were given off. After cooling, 1 cc. of the acetate buffer was added and the colorimetric measurement made as described before. In this way a solubility was found corresponding to 1.95 mg. of anhydrous lanthanum oxalate per liter. This figure is about 6% smaller than that found by the volumetric method, which is a satisfactory agreement considering the approximate character of the colorimetric reading. The following table gives a summary of the data on the solubility of lanthanum oxalate described in the literature.

SOLUBILITY OF LANTHANUM OXALATE

Mg. of Anhydrous Oxalate per Liter

Investigator	Conductivity method	Gravimetric method	Volumetric method	Colorimetric method
Rimbach and Schubert[13]	0.62			
Hauser and Herzfeld[15]	0.70	0.96	1.21	
Sarver and Brinton[16]	2.07	2.14		
Kolthoff and Elmquist	0.60		2.08	1.95

The agreement between Sarver and Brinton's gravimetric figure and our volumetric one is very satisfactory. The conductivity method undoubtedly gives much too low results, which is not surprising considering the tendency of various earth alkali oxalates to form complex ions in the solution.[17]

The Solubility of Lanthanum Oxide and Hydrous Lanthanum Oxide

Conductivity Method.—At the beginning of this paper, it was mentioned that the hydrolysis of lanthanum chloride is negligibly small. Therefore, lanthanum hydroxide

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[15] R. J. Meyer and O. Hauser, "Die Seltenen Erden und Erdsauren," p. 61.

[16] L. A. Sarver and P. H. M.-P. Brinton, THIS JOURNAL, 49, 943 (1927).

[17] Cf. R. Scholder, E. Gadenne and H. Niemann, *Ber.*, 60, 1510 (1927). Recently Mr. Sandell found in this Laboratory a much lower value for the solubility of magnesium oxalate by the conductivity method than by direct determinations and even in the case of calcium oxalate there was a small but distinct difference.

must be a strong base and the saturated, extremely dilute solution can be considered as being completely ionized.

Various products of lanthanum oxide (cf. under materials used) were added to the water which had been made carbon dioxide free in the conductivity cell. The passage of carbon dioxide-free air was continued until the conductance was constant, As a rule this was the case after one-half to three hours and then it remained constant for at least a day. If some more oxide was added to the saturated solution, the conductance did not change, which is a good proof of the absence of foreign electrolytes. As lanthanum oxide absorbs carbon dioxide very readily, the products were ignited in an electric furnace at 800" and while still hot introduced into the cell. The saturated solution of the various products had the same conductivity; after subtracting the conductivity of the carbon dioxide-free water, a value of 3.34×10^{-6} rec. ohms was found, corresponding to a solubility of 0.67 mg. of La_2O_3 per liter. For the conductance of the saturated solution of precipitated and washed hydrous lanthanum oxide a lower value was found, probably on account of a slight contamination by carbon dioxide. A solubility of 0.3 mg. of La_2O_3 per liter was derived from the conductivity figures.

Volumetric Method.—The solubilities of the three oxides and the hydrous oxides were also determined in a volumetric way. Water was made carbon dioxide free in 2.5-liter paraffin-lined bottles (the paraffin coat was washed with a solution of ammonia in 50% alcohol to remove traces of acids), the oxide or hydrous oxide was added quickly and the bottles rotated in a thermostat for ten days. After the settling of the precipitate in the thermostat, large samples were collected with a pressure pipet. One liter of each solution and the same volume of a blank were evaporated to a small volume, a known excess of 0.01 N hydrochloric acid was added, and after removing all carbon dioxide, back titrated with 0.01 N base, using brom cresol green as an indicator. The titration error was corrected for in an empirical way. In all cases it was found that 1 liter of solution required 1.29 to 1.36 cc. of 0.01 N acid for its neutralization, corresponding to a solubility of 0.73 mg. of La_2O_3 per liter. This is in satisfactory agreement with the conductimetric data considering the extremely slight solubility. W. Busch[18] found by the volumetric method a solubility of 4 mg of La_2O_3 per liter at 25°. However. he mentions that the accuracy of his method is dependent upon the rapidity and the thoroughness of the filtration. E. Sadolin[19] calculated from potentiometric determinations of PH in mixtures of lanthanum chloride and hydrous lanthanum oxide at 18° a solubility product $[La^{+++}][OH^-]^3 = 10^{-20.98}$, corresponding to a solubility of 0.405 mg. of lanthanum oxide per liter. From our figures a solubility product of aged lanthanum hydroxide of $10^{-20.04}$ is derived.

Summary

1. The mobility of the lanthanum ion at infinite dilution and at 25° is 77.
2. A colorimetric method with sodium alizarinate as reagent has been developed for the determination of traces of lanthanum.
3. At 25° the solubility of lanthanum oxalate is equal to 2.08 mg. of the anhydrous salt per liter. The conductivity method gives much too low results on account of a complex dissociation of the dissolved lanthanum oxalate.
4. The solubility of lanthanum oxide and aged hydrous lanthanum

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[18] W. Busch, *Z. anorg. allgem. Chem.*, 161, 161 (1927).

[19] E. Sadolin, *ibid.*, 160, 133 (1927).

oxide is found to be 0.7 mg. of La_2O_3 per liter at 25°. The data from the conductivity and volumetric methods agree within 10%.

MINNEAPOLIS, MINNESOTA

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

THE QUANTITATIVE DETERMINATION OF LANTHANUM BY PRECIPITATION AS OXALATE OR AS HYDROXIDE AND THE HIGHER OXIDE FORMATION OF LANTHANUM

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RECEIVED DECEMBER 22, 1930 PUBLISHED APRIL 6, 1931

The Determination of Lanthanum by Precipitation as Oxalate.—As lanthanum oxalate carries down alkali oxalates[2] oxalic acid must be used as a precipitating agent. The determination can be made volumetrically or gravimetrically. All experiments have been carried out with lanthanum chloride solutions. Pure[3] lanthanum chloride ($LaCl_3 \cdot 6H_2O$) was prepared and a standard solution of this product made up in a known weight of water. The latter was standardized by gravimetric chloride and lanthanum determinations according to precision methods, and contained 0.2946 equivalent of $LaCl_3$ per 1000 g. of solution (chloride analysis). In all further experiments a known volume was pipetted out and weighed. All reagents used were purified and tested for purity according to precision methods.

Volumetric Determination.—(a) The excess of oxalic acid is titrated in an aliquot part of the filtrate. (b) After washing out with water the precipitate is dissolved in warm dilute sulfuric acid and titrated according to the standard procedure with permanganate.

Ten-cc. portions of the stock solution of lanthanum chloride were pipetted into iodine flasks of known weight. Afterward the flasks were reweighed, varying amounts of a pure 0.05 molal oxalic acid solution were added and the flasks and contents again weighed. After standing overnight, weighed portions of the filtrates were titrated with a standard permanganate solution added from a weight buret. In all cases the titration error was determined by experiment. The precipitated lanthanum oxalate was collected on a filter and washed with cold water until the filtrate turned methyl orange the same shade as the water. The precipitate was

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[1] From a thesis submitted by Ruth Elmquist to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Th. Sheerer, Ann. *phys. chim.*, [II]56,479 (1842); G. P. Baxter and R. C. Griffin, THIS JOURNAL, 28, 1684 (1906); G. P. Baxter and H. W. Daudt, *ibid.*, 30, 563 (1908); compare next paper in this series, where an interpretation of this so-called coprecipitation has been given.

[3] *Cf.* I. M. Kolthoff and Ruth Elmquist, THIS JOURNAL, 53, 1217 (1931).

then dissolved in dilute sulfuric acid and titrated with permanganate. The results are given in Table I. From Expts. 1–4 it is evident that a relatively large excess of oxalic acid must be added in order to get a quantitative precipitation of lanthanum oxalate. Moreover, the high values in Expts. 2, 3 and 4 obtained by titrating the filtrates (Columns 4 and 5) show that oxalic acid is carried down by lanthanum oxalate, the amount increasing with the quantity of precipitant. This occlusion, however, is much less than with alkali oxalates.

In order to get good results a large excess of oxalic acid must be used in the precipitation, and the precipitate washed for a long time with water in order to remove the adsorbed oxalic acid. Even after the filtrate gives an intermediate color with methyl orange, the precipitate still contains oxalic acid and about 175 cc. more wash liquid is required to remove the last traces of oxalic acid.

Precise results are obtained according to the following procedure (Expt. 5, Table I): 50 cc. of normal oxalic acid is added to 10 cc. of the lanthanum chloride solution. The precipitate is collected and washed until the filtrate turns methyl orange the same shade as that of the wash water. The lanthanum oxalate is dissolved and titrated. The results are accurate to 0.1%.

Experiments 5 (Table I) have been carried out according to the above procedure; 275 cc. of water was used to wash out all the oxalic acid. As the solubility of lanthanum oxalate in water amounts to 0.033 milliequivalent per liter,[3] the error due to solubility in our case cannot be greater than 0.2%, and in reality it was much smaller, since the filtration was rapid and permitted only momentary contact between liquor and precipitate.

TABLE I

VOLUMETRIC DETERMINATION OF LANTHANUM BY PRECIPITATION AS OXALATE

Expt.	M. equiv. La taken	M. equiv. oxalic acid added	M. equiv. La found from titration of filtrate	Deviation from calcd. value, %	M. equiv. La found from titratiou of ppt.	Deviation from calcd. value, %
1	2.990	4.332	2.960	−1.00	2.951	−1.30
2	2.996	5.005	3.002	+0.20	2.990	−0.20
3	2.999	7.508	3.016	+ .57	3.012	+ .43
4	2.989	10.201	3.133	+4.81	2.984	− .17
5a	2.993	50			2.991	− .07
5b	2.994	50			2.995	+ .03
5c	2.992	50			2.988	− .13

In the literature[4] it is reported that the volumetric determination of lanthanum by titration of the lanthanum oxalate gives high results. This must be attributed to an incomplete removal of oxalic acid from the precipitate.

[4] G. Krüss and A. Loose, *Z. anorg. Chem.*, 4, 161 (1893); W. A. Drushel, *Am. J. Sci.*, [IV] 24,197 (1907).

Since sodium oxalate (and other alkali oxalates) are carried down to a considerable extent by lanthanum oxalate and cannot be removed by washing the precipitate, the experiments described in Table I have been repeated in the presence of 2 and 3 g. of sodium chloride added as a 1 *N* solution. The results showed a slight coprecipitation of sodium oxalate or bioxalate. According to the precise procedure (Expt. 5) the results were accurate to within 0.2%.

The Gravimetric Determination of Lanthanum by Precipitation as Oxalate.—Twenty-five to 100 cc. of a 1 *N* oxalic acid solution was added to 10 or 40 cc. of the standard lanthanum solution (weighed portion) with constant stirring. After standing overnight the precipitate was filtered, washed and dried at temperatures between 50 and 300°. No temperature was found at which any hydrate of lanthanum oxalate reached constant weight. The oxalate decomposes before the last portion of the water has been removed.[5] Therefore the filter and precipitate were ignited in an electric furnace, in which the oxalate was transformed into oxide. It was found that the lanthanum oxide absorbs water from the atmosphere very readily. When the relative humidity of the air is low (about 20%), the oxide does not increase in weight during the weighing, but when it is high (60% or more) its weight increases rapidly when the oxide is exposed to the air. Therefore for accurate work it is recommended that the crucible containing the oxide, after being cooled in a desiccator, be weighed in a weighing bottle with well-fitted cover. At 700° the oxide is slow in coming to constant weight; after heating for twenty-four hours at this temperature the weight was 6% too high. This result is not in harmony with the statement of Racker and Klaassens,[5] who find that on heating lanthanum oxalate the formation of the oxide is quantitative at 600°. It was found that after heating the oxalate for five to eight hours at temperatures between 800 and 900°, a quantitative formation of the oxide takes place; the weight does not change upon prolonged heating at these temperatures. It is recommended that the ignition temperatures should not exceed 850°; at 1000°, the oxide, after having reached a minimum weight, increases its weight upon further heating. A similar phenomenon has been noted by P. H. M.-P. Brinton and L. A. Sarver,[6] though they did not investigate the influence of the temperature upon this effect. It is possible to obtain perfectly constant results if the ignition temperature is kept between 800 and 850°.

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[5] After this work was finished, a paper was published by H. J. Backer and K. H. Klaassens, *Z. anal. Chem.*. 81, 104 (1930). These authors state that at 250" lanthanum oxalate is obtained in the anhydrous form and that the weight is constant. At temperatures above 300" they noticed a decomposition of the oxalate under evolution of carbon monoxide and carbon dioxide. Between 400 and 500° again a constant weight was found, corresponding to the composition La_2CO_5 (basic carbonate), and it is recommended that this compound be used as a weighing form of lanthanum oxalate.

[6] Sarver and Brinton, THIS JOURNAL, 49, 943 (1927).

The results given in Table II were obtained by weighing the crucible containing the oxide in a closed weighing bottle after constant weight had been attained at 800°.

TABLE II

GRAVIMETRIC DETERMINATION OF LANTHANUM BY PRECIPITATION AS OXALATE AND WEIGHING AS OXIDE

M. equiv. La taken	M. equiv. $H_2C_2O_4$ added	M. equiv. La found	Deviation from theoretical value, %
10.425	100	10.453	+0.25
11.684	100	11.698	+ .15
11.691	100	11.713	+ .19
11.639	100	11.658	+ .16
11.609	100	11.625	+ .14

The results are consistently 0.15% high. Comparing the results with those reported in Table I (5a, 5b and 5c) it may be inferred that the volumetric method gives more precise results. As the latter is much easier to perform, and gives results in a much shorter time it is preferable to the gravimetric method.

The Determination of Lanthanum by Precipitation as Hydrous Oxide

Volumetric Determination.—Though lanthanum hydroxide behaves like a strong base, its solubility in water is so small that the saturated solution does not react alkaline to thymolphthalein as indicator. Therefore the direct titration of lanthanum chloride with sodium hydroxide (or with an excess of the latter and back titration) was tried using thymolphthalein as an indicator. The end-points were indistinct and the results very unsatisfactory. Later the interesting fact was found that a suspension of lanthanum oxide in water assumes a dark blue-violet color upon addition of thymolphthalein, though the clear saturated solution remains colorless. The indicator is hydrolytically adsorbed by the solid strong base.

In the following experiments a weighed portion of a standard 0.05 N sodium hydroxide solution (carbonate free, kept in paraffin-coated flasks) was added to a weighed amount of the stock solution of lanthanum chloride. The next day weighed portions of the filtrate (the first few cc. were discarded) were titrated with 0.05 N hydrochloric acid, using methyl orange as an indicator. The acid and base were standardized according to precision methods, and the titration error was corrected for in an experimental way. In all experiments weight burets were used. The precipitates were washed with a mixture of 50% alcohol and water until the wash liquid was free from alkali when tested with phenol red. They were then dissolved in a weighed excess of standard acid and the excess titrated back.

As shown by Expts. 1 and 2 in Table III, the results are low. The deviation is due to basic chloride formation, which was proved by quantitative chloride determinations in the filtrate and in the precipitate. Better results might be expected if the lanthanum chloride were added slowly to an excess of sodium hydroxide. Experiments **3, 4, 5** and **6** in Table III were carried out in this way. The last two experiments show that good results are obtained if the lanthanum solution is added slowly to a large excess of sodium hydroxide (about five times the theoretical amount) and the precipitate is titrated after having been washed with a mixture of 50% alcohol and water. No basic chloride is formed. The chloride in the filtrates and wash liquids of Expts. 5 and 6 was determined gravimetrically; the results were 0.10 and 0.15% higher than the theoretical figures.

TABLE III

VOLUMETRIC DETERMINATION OF LANTHANUM BY PRECIPITATION AS HYDROXIDE

Expt.	M. equiv. La taken	M. equiv. NaOH added	M. equiv. La found from filtrate	Deviation from calcd. value, %	M. equiv. La found from titration of ppt.	Deviation from calcd. value, %
1	2.985	3.179	2.897	−2.95	2.891	−3.15
2	2.999	4.974	2.941	−1.93	2.950	−1.63
3	3.001	3.185	2.957	−1.47	2.978	−0.77
4	2.989	4.287	2.951	−1.27	2.973	− .54
5	2.984	15	...	....	2.986	+ .13
6	3.001	15	...	....	3.007	+ .20

Precipitation **of** the Hydrous Oxide by an Excess **of Ammonia.**—Carbonate-free ammonia was prepared by distillation over calcium oxide and the solution was kept in a paraffin-coated flask. An excess of ammonia was added to the lanthanum chloride solution and the precipitate after having been washed was titrated in the way described. In all cases the results were low on account of basic chloride formation, the deviation being larger when the ammonia was added to a hot solution of lanthanum chloride than at room temperature. The speed of addition of ammonia has also an influence; the results are better when it is added quickly (deviation in the various cases between **1.5** and 3.8% from the theoretical value). By gravimetric chloride determinations it was found that no basic chloride is formed when lanthanum chloride is added slowly to an excess of ammonium hydroxide. A series of experiments was next run in which **10** cc. (weighed portion) of the approximately **0.3** *N* lanthanum chloride was added slowly to about **30** to **40** cc. of **1** N ammonia. The precipitate was collected the next day and washed with a mixture of **50%** alcohol and water until free from ammonia. The results obtained agreed within 0.1% with the theoretical figures.

Gravimetric Determination.—Since it was found that the last procedure gives a quantitative precipitation of hydrous lanthanum oxide free from chloride, 40-cc. weighed portions of the approximately **0.3** *N* lanthanum chloride stock solution were added with constant stirring to about 80 to 100 cc. of N ammonia. The next day the precipitates were filtered and washed with a dilute solution of ammonium hydroxide to decrease the solubility. After ignition to constant weight in an electric furnace at 800°, the precipitate was weighed in a closed weighing bottle.

The results are accurate within 0.3% as indicated by the figures in Table IV.

TABLE IV

GRAVIMETRIC DETERMINATION OF LANTHANUM BY PRECIPITATION AS HYDROUS OXIDE BY AMMONIA

M. equiv. La taken	M. equiv. La found	Dev. from calcd. value, %
11.666	11.674	+0.07
11.633	11.657	+ .21
11.574	11.610	+ .30
11.619	11.656	+ .3
11.648	11.673	+ .22

T. O. Smith and C. James[7] found higher results when they precipitated lanthanum chloride with sodium hydroxide and ignited to oxide than when they used the oxalic acid method. With ammonium hydroxide the results were found to lie between the two. This can be easily explained by the formation of a basic chloride in the direct precipitation with base.

Higher Oxide Formation of Lanthanum.—In the discussion of the gravimetric determination of lanthanum reference has been made to an increase in weight obtained upon the ignition of lanthanum oxide at high temperature. This phenomenon was first noted by R. Hermann,[8] who reported a gain of 0.24%. H. Tschiesche[9] however, found no variation in weight upon heating lanthanum oxide and decided that Hermann's results were erroneous. Neither investigator reported the temperature at which the ignitions were made. Sarver and Brinton[6] next observed that lanthanum oxide shows a well-defined tendency to descend to a minimum in weight and then to register small gains of approximately 0.1 to 0.2 mg. upon subsequent ignitions. After heating lanthanum oxide for three hours at 500° under a pressure of 300 pounds, H. A. Pagel and P. H. M.-P. Brinton[10] found an increase in weight of only 0.02%. They concluded that no higher oxide of lanthanum exists. On the other hand, P. Melikoff and L. Pissarjewsky[11] report having obtained a peroxide to which they assigned the formula $La_2O_5 \cdot xH_2O$ by adding hydrogen peroxide and potassium hydroxide to solutions of lanthanum nitrate.

Since the work described in the present paper indicated the existence of a higher oxide, an extensive study of its formation at high temperatures has been made. Though it has not been possible to find the exact con-

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[7] Smith and James, THIS JOURNAL, 36, 909 (1914).

[8] Hermann, *J. prakt. Chem.*, 82, 385 (1861).

[9] Tschiesche, *ibid.*, 107, 65 (1869).

[10] Pagel and Brinton, THIS JOURNAL, 51, 42 (1929).

[11] Melikoff and Pissarjewsky, *Z. anorg. Chem.*, 21, 70 (1899).

ditions (temperature) at which it is formed, there is hardly any doubt that peroxides are formed when lanthanum oxide is ignited at very high temperatures in the air.[12]

The results described in Table V have been obtained by heating lanthanum oxide at various temperatures in an electric muffle furnace (gas burners should be avoided, as the oxide will be contaminated by sulfur trioxide upon long heating). The oxide was obtained from hydrous lanthanum oxide, the latter being prepared by slowly adding a solution of lanthanum chloride to an excess of ammonia. The precipitate was ignited at 800° to constant weight.

The experiments have been carried out with five different samples of lanthanum oxide. In all cases an increase in weight amounting to 10.2 to 10.8% was noticed upon prolonged ignition at white heat. Identical results were obtained with lanthanum oxide obtained from the oxalate.

If the sesquioxide were converted into the higher oxide, La_2O_5, an increase in weight of 9.81% would result.

TABLE V

INCREASE IN WEIGHT OF LANTHANUM OXIDE UPON HEATING AT HIGH TEMPERATURES

Time, hours	Condition	Increase in weight of 0.1655 La_2O_3 in %	Increase in weight of 0.2585 g. of La_2O_3 in %
10	Red heat	0.0	0.0
5	Light red heat	.0	.0
14	Light red heat	1.03	1.21
14	White heat	1.94	7.34
14	White heat	9.45	8.85
18	White heat	10.06	9.88
12	White heat	10.48	10.25
15	White heat	10.48	10.26

In other experiments three different types of oxide were used: one from hydrous oxide, one from oxalate and one from pure lanthanum nitrate. Another muffle furnace was used, as the former was burned out. After a long period of heating at white heat the increase in weight was 18.5 to 19.7%. These values closely check the theoretical gain in weight (19.63%) which would result if the higher oxide La_2O_7 were formed.

Four other sets of experiments were run in which the temperature was measured by means of an electric pyrometer. The results were irregular; after an increase in weight of 5.65% had been noticed, the increase in weight dropped again to about 2% on longer heating. It seems that the formation of higher oxide is slow at temperatures of 1100". Other furnaces were built; the addition of a trace of a cerium salt[13] and of platinum salt

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[12] For a detailed discussion of all experiments, see thesis of Ruth Elmquist, pp. 73-88.

[13] R. Marc, *Ber.*, 35, 2370 (1902), stated that the presence of a trace of cerium catalyzes the higher oxide formation of praseodymium.

as a catalyst was tried,[14] but at present no definite information on the conditions of formation of the higher oxide has been obtained.

The results so far, however, show definitely that lanthanum oxide heated for long periods of time at very high temperature in an electric furnace and exposed to the air can be transformed into the higher oxides La_2O_5 and La_2O_7.

Summary

1. A precise volumetric procedure has been described for the determination of lanthanum as lanthanum oxalate. The oxalate can be estimated gravimetrically as oxide if ignited to constant weight in an electric furnace at 800 to 900° and weighed in a well-closed weighing bottle.
2. In the precipitation of lanthanum chloride with sodium hydroxide or ammonia basic chloride is formed. This is avoided by adding the lanthanum solution slowly to an excess of the base. Use of this fact is made in the volumetric and gravimetric determinations of lanthanum by precipitation as hydrous oxide.
3. Lanthanum oxide heated for long periods of time at white heat in an electric muffle furnace in air can be transformed into higher oxides La_2O_5 and La_2O_7.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OP THE UNIVERSITY OR MINNESOTA]

LANTHANUM ALKALI OXALATES[1]

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RECEIVED DECEMBER 22, 1930 PUBLISHED APRIL 6, 1931

The fact that alkali oxalates are carried down by lanthanum oxalate was first observed by Th. Sheerer.[2] G. P. Baxter and R. C. Griffin[3] stated that ammonium oxalate, but not oxalic acid, was carried down in considerable quantities by rare earth oxalates and that occlusion of ammonium oxalate was made negligible by acidifying the solution with twice the equivalent amount of nitric acid. G. P. Baxter and H. W. Daudt[4] reported that potassium oxalate was occluded to the same extent as ammonium oxalate (5–18%) but that sodium oxalate was occluded only slightly even in neutral solution. Since the occluded oxalate was determined after washing the lanthanum oxalate, part of the occluded salt may be removed from the precipitate. For this reason a series of experi-

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[14] Ref. 12, p. 82–87.

[1] From a thesis submitted by Ruth Elmquist to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Sheerer, Ann. *phys. chim.*, [II] 56,479 (1842).

[3] Baxter and Griffin, THIS JOURNAL, 28,1684 (1906).

[4] Baxter and Daudt, *ibid.*, 30, 563 (1908).

ments was carried out in which an excess of alkali oxalate was added to a lanthanum chloride solution. The excess of oxalate was determined in an aliquot part of the filtrate by titration with potassium permanganate. The precipitates obtained with ammonium oxalate were washed out with distilled water containing a trace of potassium sulfate in order to prevent them from going into colloidal solution, and after dissolving in warm sulfuric acid titrated with permanganate. The procedure was the same as that described in a previous paper[5] for the experiments with oxalic acid. As may be seen from the results in Table I, the greater part of the alkali oxalate carried down by lanthanum oxalate is removed by washing out. The low results obtained with sodium and potassium oxalate which are given in the last column are explained by the fact that at the end of the washing a trace of the precipitate ran through the filter in a colloidal state.

TABLE I

COPRECIPITATION OF ALKALI OXALATES BY LANTHANUM OXALATE

Preciuitant oxalate	M. equiv. of $LaCl_3$ taken	M. equiv. of oxalate added	Equiv. of alkali oxalate carried down by 100 equivs. of lanthanum oxalate	Equiv. of alkali oxalate in 100 equivs. of the ppt. after washing out
Sodium	2.999	4.024	5.53	(−1.10)
Sodium	2.990	7.555	15.15	(−0.27)
Potassium	2.993	3.993	13.1	(− .90)
Potassium	2.991	7.487	48.2	(− .50)
Potassium	2.986	9.983	66.5	(−1.2)
Ammonium	2.993	3.982	18.5	+2.2
Ammonium	2.992	9.954	33.0	+3.6

The order of the coprecipitation found is potassium oxalate > sodium oxalate > ammonium oxalate.

This carrying down of alkali oxalates can be explained as due to the ordinary causes of coprecipitation or by the formation of definite double salts of lanthanum oxalate with alkali oxalate. The large extent to which the alkali oxalates are carried down indicates double salt formation. No double oxalates of the[4]cerium group of rare earth elements have been described in the literature;[6] the following study, however, shows that even at relatively low concentrations of alkali oxalates in the solution lanthanum oxalate is transformed into a double salt. In the present investigation weighed amounts of lanthanum oxalate were shaken in paraffined oil bottles in a thermostat at 25° with 75 to 100 cc. portions of solution of ammonium oxalate, sodium oxalate and potassium oxalate of various but known concentrations. After shaking for a definite time the bottles were clamped in

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[5] Kolthoff and Elmquist, THIS JOURNAL, 53, 1225 (1931).

[6] Double alkali oxalates of the yttrium group of rare earth elements are known; see P. T. Cleve and O. Hoeglund, Bull. *soc. chim.*, *18*, 289 (1872); C. A. von Welsbach, *Monatsh.*, 27,935 (1906); L. A. Pratt and C. James, THIS JOURNAL, **34,488** (1911).

an upright position in the thermostat. Although a few samples settled quickly, considerable difficulty was usually experienced in removing the suspended solid from the solution. Filtration through various materials gave opalescent filtrates. The best method for obtaining a clear solution was to place the oil bottles in which the experiments were made in a centrifuge. They were rotated for several minutes and the clear solution removed by cautious pipetting with slow mechanical suction. Every sample was examined for suspended solid and discarded if any was found. Aliquot portions of both samples and blanks were titrated with permanganate. From the difference in concentration the number of moles of alkali oxalate removed by one mole of lanthanum oxalate was calculated.

The lanthanum oxalate used was prepared by precipitating a pure lanthanum chloride solution with an excess of oxalic acid. The precipitate was washed with distilled water until methyl orange gave the wash liquid the same color that it gives to the water. The lanthanum oxalate was air-dried and analyzed by titrating with a standard solution of potassium permanganate (weight buret) just before the shaking experiments were started. The results are given in the tables. The formation of the double salts is very slow, especially at low concentrations of alkali oxalate; in some cases equilibrium had not been attained even after four weeks of shaking.

Discussion of the Results.—Even at low concentrations of alkali oxalates, lanthanum oxalate is slowly transformed into a double salt of the general composition $1La_2Ox_3 \cdot 1Alk_2Ox \cdot xH_2O$ (1:1 compound). At concentrations of ammonium oxalate smaller than 0.012 *N*, lanthanum oxalate is the stable solid body; at higher concentrations it is transformed into the double salt 1:1 (Table II, Expts. 3 and 4). At a concentration of

TABLE II

DOUBLE SALT FORMATION OF LANTHANUM OXALATE WITH AMMONIUM OXALATE

Expt.	Initial concn. of Am_2Ox N	Final concn. of Am_2Ox, N	Vol. of soln. shaken, cc.	Millimoles of La_2Ox_3 taken	Time shaken, weeks	Moles of Am_2Ox removed by 1 mole of La_2Ox_3
1	0.01	0.01	75	0.4155	5	0.00
2	.01	.01	75	.4194	7	.01
3	.0191	.0122	75	.6925	5	.37
4	.0191	.0120	75	.6884	7	.39
5	.0302	.0128	75	.6840	5	.95
6	.0302	.0126	75	.6881	7	.96
7	.0291	.0215	100	.412	1	.92
8	.0432	.0292	100	.692	4	1.02
9	.0693	.0553	100	.683	1	1.02
10	.0996	.0861	100	.679	1	1.00
11	.1990	.1722	100	1.366	1	0.98
12	.3905	.3637	100	1.366	1	.98
13	.5279	.5144	100	0.692	4	.98
14	.5442	.5315	100	.692	4	.92

TABLE III

DOUBLE SALT FORMATION OF LANTHANUM OXALATE WITH POTASSIUM OXALATE

Expt.	Initial concn. of K_2Ox, N	Final concn. of K_2Ox, N	Vol. of soln. shaken, cc.	Millimoles of La_2Ox_3 taken	Time shaken, weeks	Moles of K_2Ox removed by 1 mole of La_2Ox_3
1	0.0101	0.0101	75	0.4159	5	0.00
2	.0101	.00922	75	.4118	7	.11
3	.0281	.0279	100	.679	1	.016
4	.0293	.0162	100	.692	4	.95
5	.0483	.0349	100	.679	1	.99
6	.0682	.0556	100	.683	1	.93
7	.0985	.0849	100	.679	1	1.00
8	.1406	.1259	100	.692	4	1.06
9	.1470	.1220	100	.684	4	1.83
10	.1989	.1466	100	1.366	1	1.92
11	.2993	.2476	100	1.366	1	1.90
12	.3990	.3460	100	1.366	1	1.95
13	.4978	.4708	100	0.679	1	1.99
14	.9915	.8858	100	2.730	1	1.94
15	1.718	1.662	100	1.372	1	2.01
16	3.853	3.745	100	1.366	1	1.96

TABLE IV

DOUBLE SALT FORMATION OF LANTHANUM OXALATE WITH SODIUM OXALATE

Expt.	Initial concn. of Na_2Ox, N	Final concn. of Na_2Ox, N	Vol. of soln., shaken, cc.	Millimoles of La_2Ox_3 taken	Time. shaken, weeks	Moles of Na_2Ox removed by 1 mole of La_2Ox_3
1	0.01	0.01	75	0.4120	5	0.00
2	.01	.01	75	.4145	7	.00
3	.02	.02	75	.4190	7	.00
4	.0374	.0216	100	.692	4	1.14
5	.0498	.0363	100	.692	4	0.99
6	.1002	.0866	100	.679	1	1.00
7	.1985	.1851	100	.679	1	0.99
8	.2372	.2233	100	.692	4	1.01
9	.2449	.2263	100	.692	4	1.34
10	.2479	.2249	100	.692	4	1.66
11	.3014	.2716	100	.692	4	1.96
12	.4012	.3492	100	1.366	1	1.90
13	.4993	.4721	100	0.679	1	2.00

about 0.01 N potassium oxalate both lanthanum oxalate and the double salt 1:1 can exist as solid bodies, whereas the former seems to be stable in sodium oxalate solutions up to a concentration of about 0.02 N Na_2Ox.

It is desirable to determine the equilibrium concentration of alkali oxalate at which lanthanum oxalate and the double compound 1:1 can exist as solid bodies from the other side by starting with the double salt. As the formation of the double salt, especially at relatively low oxalate concentrations, is slow, it is not quite certain whether in all cases equilibrium had been attained even after shaking for seven weeks.

Sodium and potassium oxalate can form two kinds of double salts, $La_2Ox_3 \cdot 1K_2(Na_2)Ox \cdot xH_2O$ and $La_2Ox_3 \cdot 2K_2(Na_2)Ox \cdot yH_2O$. Both solid phases are in equilibrium with the solution at a potassium oxalate concentration of 0.125 N (Table III, Expts. 8 and 9) or a sodium oxalate concentration of 0.225 *N* (Table IV, Expts. 9 and 10). No indication has been obtained that a similar compound 1:2 of ammonium oxalate exists.

Lanthanum oxalate was also shaken with solutions of oxalic acid of concentrations varying between 0.01 and 1.01 N. After shaking for a few weeks the filtrates were analyzed by titration with sodium hydroxide and with permanganate. Under no conditions was there a double compound formation. At higher oxalic acid concentrations (0.1 *N)* a slight adsorption of the acid by the lanthanum oxalate of the order of one equivalent per cent. was found.

The above results explain why oxalic acid and not alkali oxalates must be used as a precipitant in the determination of lanthanum.

Summary

The so-called coprecipitation of alkali oxalate with lanthanum oxalate is to be attributed to a double salt formation. Lanthanum oxalate is in equilibrium with the double salt $La_2Ox_3 \cdot (Alk)_2Ox \cdot xH_2O$ at a concentration of about 0.012 N ammonium oxalate, 0.01 *N* potassium oxalate or 0.02 N sodium oxalate.

Potassium and sodium oxalate also form double salts of the composition $La_2Ox_3 \cdot 2K_2(Na_2)Ox \cdot yH_2O$ at a concentration of 0.125 N potassium oxalate and 0.225 N sodium oxalate, respectively. No double compounds of lanthanum oxalate and oxalic acid are formed.

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

THE DECOMPOSITION OF HYDROCARBONS IN THE POSITIVE RAY TUBE

BY H. R. STEWART AND A. R. OLSON

RECEIVED DECEMBER 27, 1930 PUBLISHED APRIL 6, 1931

Some time ago, Olson and Meyers[1] investigated the reactions produced by excited mercury atoms in mixtures of hydrogen and ethylene. The products were analyzed by Dr. H. M. Kvalnes using the positive ray apparatus which Dr. Hogness and his students had constructed. By making some assumptions which were stated in the above paper, Olson and Meyers were able to postulate a reaction mechanism which accounted for the results of the analysis. The desirability of determining the trustworthiness of such an analysis was discussed privately at that time, but the actual investigation had to be postponed until a new apparatus could be built.

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[1] Olson and Meyers, THIS JOURNAL, 49, 3131 (1927).

The apparatus which was constructed was quite similar to that used by Hogness and Lunn.[2] Known mixtures of methane and ethane, which had not been exposed to light from the mercury arc, were analyzed. The results seemed to justify the assumptions made by Olson and Meyers.

Benzene and hydrogen were then exposed to the arc in the usual way. Benzene was selected so that there would no longer be a ratio of unity between the number of moles of hydrogen and the number of moles of product formed by hydrogenation. On analysis of the product in the positive ray apparatus, a complex set of peaks was obtained which indicated that benzene was broken up in the photochemical reaction. However, when pure benzene was used for analysis, lower molecular weight peaks corresponding to some of those found with the reaction product were present. This result, coupled with the results of the analysis of methane-ethane mixtures mentioned above, raised two questions: how complex can a molecule be and not be decomposed in the positive ray analysis, and what is the cause of the disruption?

Pure hydrocarbons up to and including hexane were then prepared. These substances were distilled repeatedly and the first and last fractions rejected. Positive ray analyses were then made of each hydrocarbon. Peaks due to ions of carbon chains shorter than the original were found in every case except that of methane. These peaks were too high for them to be ascribed to impurities. (Additional evidence for the purity of the original hydrocarbons is offered later.) The peak due to methane as a decomposition product is always small, accounting for the satisfactory analyses of the methane–ethane mixtures.

Hexane, at a pressure of about 10 cm., was then exposed to a hot filament of the type used in the positive ray tube (Western Electric low temperature filament) for some hours, and analyzed. The low molecular weight peaks were higher than for untreated hexane, showing that thermal decomposition by the filament was at least in part responsible for the presence of foreign substances with shorter chains.

A new tube was then constructed in such a way as to minimize thermal decomposition. In this tube (see Fig. 1) the top of the copper-plated iron ionization chamber was closed over with a copper disk soldered in place, and provided with a slot and sliding jaws. These jaws were adjusted to form a narrow slit (0.08 × 4 mm.) just below the filament and opening into the ionization chamber. The base of the chamber was closed off from the filament space by a glass sleeve fastened to the metal with cement. Two very high capacity mercury vapor pumps, each backed by an ordinary mercury vapor pump and an oil pump in turn, were connected, one to the filament chamber and the other to the magnetic deflection chamber, through large diameter tubing. The gas under analysis was introduced

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[2] Hogness and Lunn, *Phys. Rev.*, **26**, 44 (1925).

into the ionization chamber by a glass tube entering through the base. The diagram in Fig. 2 will make clear the pressure relationships.

Preliminary runs showed that the pressure in the filament chamber and deflection chamber could be maintained at 10^{-5} mm. when the pressure in the ionization chamber was 10^{-2} mm Since the field between the filament and the first slit is accelerating for electrons, any positive ions formed between the filament and the slit will be thrown back toward the filament. No negative ions have ever been detected in the ionization chamber with this tube. Due to the pressure gradient, it does not seem likely that any decomposition products formed by the filament can be present in the ionization chamber at a pressure high enough to be important. *Yet runs with the pure hydrocarbons (to hexane) showed in every case a peak for every hydrocarbon up to and including the one introduced.* The peaks were just as well marked as those obtained with the original tube, in which the bare filament was in direct contact with the gas to be ionized, and no pumping took place except through the bottom slit. Methane, which in the old apparatus gave peaks for ions of masses 12, **13,** 14, **15** and 16, showed peaks only for **15** and 16 in the new tube, in agreement with the results obtained by Hogness and Kvalnes[3] after they had succeeded in minimizing thermal decomposition.

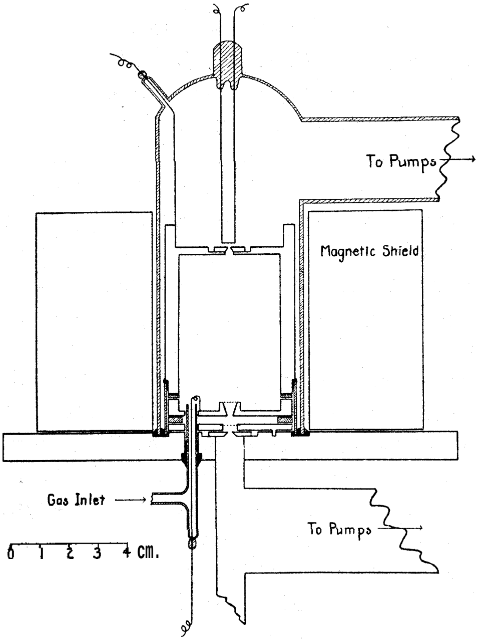

Fig. 1.—Positive ray tube. Base plate and deflection chamber are of brass. Metal parts within tube are of soft iron, copper plated. Tube proper and insulating rings (shaded) are of glass.

As will be seen later, the relative heights of the peaks vary with pressure in such a way in the range investigated (1×10^{-3} mm. to 100×10^{-3} mm.) that it is difficult to account for them as being due to secondary reactions between ions and molecules in the ionization chamber. Calculation readily shows that multiple ionization cannot account for the appearance of peaks at all of the positions of ions of the lower molecular weight hydrocarbons. For example, propane should give ions of apparent masses 44,

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[3] **Hogness and Kvalnes,** *Phys. Rev.*, **32,** 942 **(1928).**

22, 15, corresponding to $C_3H_8^+$, $C_3H_8^{++}$, $C_3H_8^{+++}$, but 22 does not appear on the curves, thus making it very unlikely that any of the ions ascribed to CH_3^+ are due to $C_3H_8^{+++}$.

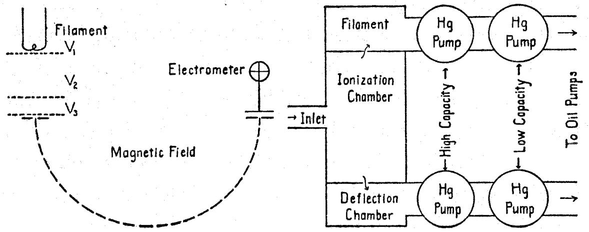

Fig. 2.—Pressure and field diagrams.

Another possibility is that ions of the original hydrocarbon are being disrupted by collision near the bottom slit, after having been accelerated in the high voltage field, and that the separate (charged) portions are being deflected in the magnetic field, thus appearing at false m/e positions. It can be shown that if an ion of mass m_1 and charge c_1 becomes an ion of mass m_2 and charge c_2, after having acquired nearly its final velocity, then the resulting ion will appear at a position given by the equation

$$\left(\frac{m}{e}\right)_2 = \left(\frac{c_1}{c_2} \times \frac{m_2}{m_1}\right)^2 \left(\frac{m}{e}\right)_1$$

Calculation again shows that the positions of the observed peaks cannot be accounted for in this way. In addition, even if positions corresponded, it would be very difficult to account for the relative intensities by such a process, for it is necessary that the ions be broken up by collision without being deviated appreciably from their original path. Peaks of this type have been reported only once, by Smyth[4] in the case of hydrogen.

There seems to be only one alternative, that the ionizing electrons decompose the hydrocarbons on impact, and this will be studied in the remainder of this paper.

Positive Ray Analysis of Propane and Butane

Series of runs were made with pure propane and with pure butane, over a range of pressures. The results of typical runs are shown in Fig. 3. In this figure, the ordinates represent electrometer deflections, and the abscissas are proportional to the current through the magnet, but for convenience each peak is labeled with the calculated m/e value of the corresponding singly charged ion. Due to the great range of mass which it was necessary to cover in a single run, it was found convenient to fix the accelerating voltage V at a suitable value (in these runs, 1200 volts) and vary the magnetic field.

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[4] Smyth, *Phys. Rev.*, *25*, 452 (1925).

There is no question of the purity of the gases employed. As was mentioned previously, they were dried and distilled repeatedly, with rejection of the first and last portions. As a final test, the positions of the peaks in separate runs on methane, ethane, propane and butane were compared. Note, in Fig. **3**, that in the case of butane, CH_4^+, $C_2H_6^+$ and $C_3H_8^+$ are missing; that in the case of propane, while $C_3H_8^+$ is present, $C_2H_6^+$ and CH_4^+ are missing. In ethane one finds $C_2H_6^+$ but not CH_4^+. The peak corresponding to mass 16 (CH_4^+) never appeared except when methane had been intentionally introduced. If the peaks for the hydrocarbons lower in molecular weight than the one introduced were due to their presence as impurities, a peak for the corresponding saturated ion would be present, and this is found not to be the case.

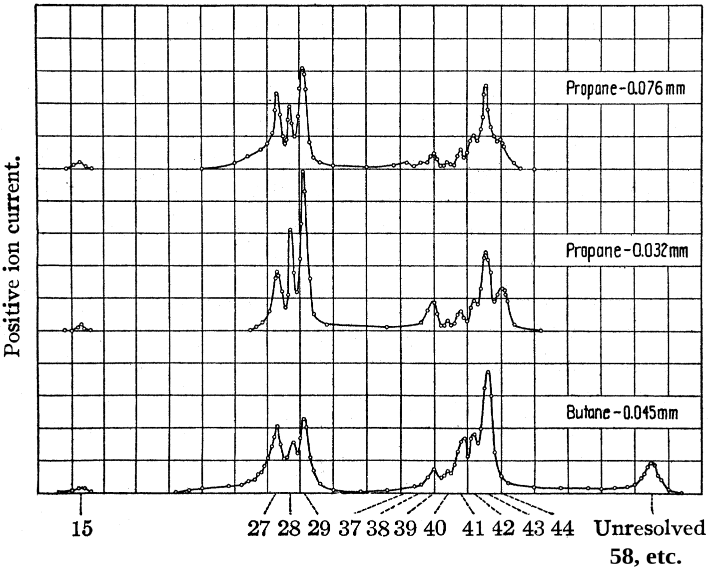

Fig. 3.—Typical runs with propane and butane. Ordinates represent electrometer deflections; abscissas, current through the magnet. Numbers given are calculated masses of corresponding singly charged ions.

The results for propane and butane are given in the accompanying tables, which summarize the peak heights (in one case the areas under the peaks) for various pressures. The policy of measuring the total areas under the curves for ions having the same number of carbon atoms but varying amounts of hydrogen, was adopted for butane on account of the lack of resolution at higher pressures and molecular weights. It can be shown that the geometrical resolving power of the apparatus is ample, and that the lack of complete resolution is due to other causes.

The tables also include a tabulation of the relative proportions of the several types of carbon chains present as ions, calculated from the previous data, and plotted in Figs. 4 and 5. In order to restrict attention to **the** features of the data which it is desired to discuss, and to avoid complicating

TABLE I

Propane. 10-Volt Collecting Field (V_2). Heights of Peaks

Press., mm. × 10^3	C	C_2			C_3				
10	1.5	15	25	42	5	4	4	15	11
20	1.5	17	23	41	7	5	3	14	7
32	2	23	39	65	11	8	11	31	17
51	3	36	44	73	13	14	19	45	18
76	2	29	25	39	6	8	13	32	11
104	1.5	14	13	22	6	7	8	29	9

Propane. 90-Volt Collecting Field (V_2). Heights of Peaks

Press., mm. × 10^3	C	C_2		C_3		
8.5	0.8	7.0	15.5	3.5	4.3	7.0
12.4	2.0	24.8	34.8	8.8	15.8	14.7
30	1.5	23.5	32.5	9.8	17.0	17.5
57	3.0	30.0	32.0	11.5	18.5	18.0
83	6.5	32.5	28.0	11.5	18.5	17.5

The peaks of the above set of runs were only partially resolved, and the "background" very high, on account of the high collecting field.

Butane. 10-Volt Collecting Field (V_2). Areas under Peaks

Press., mm. × 10^3	C	C_2	C_3	C_4
13	1.2	44	77	11
27	2.5	77	114	20
45	4.0	111	140	30
60	5.6	126	133	39
81	10.4	161	135	48
100	2.7	100	67	18

TABLE II

Propane. 10-Volt Collecting Field. Percentages (Figs. 4 and 5)

Press., mm. × 10^3	C	C_2	C_3	$C_2H_3^+$	$C_2H_4^+$	$C_2H_5^+$
10	1.3	67.2	31.5	18.3	30.5	51.2
20	1.8	68.0	30.2	21.0	28.4	50.6
32	1.3	61.3	37.4	18.1	30.7	51.2
51	1.0	57.8	41.2	23.5	28.8	47.8
76	1.6	56.3	42.1	31.2	26.9	41.9
104	1.8	45.0	53.2	28.6	26.5	44.9

Propane. 90-Volt Collecting Field. Percentages (Fig. 4)

Press., mm. × 10^3	C	C_2	C_3
8.5	2.1	59.1	38.6
12.4	2.2	59.1	38.9
30	1.4	58.9	39.5
57	2.7	55.0	41.9
83	5.7	52.5	41.6

Table II (*Concluded*)

Butane. 10-Volt Collecting Field. Percentages (Fig. 5)

Press., mm. × 10^3	C	C_2	Ca	C_4
13	0.9	33.0	57.8	8.3
27	1.2	36.0	53.3	9.5
45	1.4	38.9	49.2	10.5
60	1.8	41.4	43.8	11.7
81	2.9	45.5	38.2	13.5
100	1.4	53.2	35 6	9.6

the diagrams, all ions containing the same number of carbon atoms are plotted as a single species, and designated by the symbols C_1, C_2, C_3, C_4.

Discussion

It has been customary in the past to ascribe progressive variations of the percentage of a given ion species with pressure to secondary reactions involving that ion. However, since the simple ion of the hydrocarbon introduced does not approach 100% as the pressure is decreased, it is apparent that in addition to ionization, other primary processes must be operative. Thermal decomposition cannot be responsible for these reactions, not only because of the evidence we have already presented, but also because the percentage of higher molecular weight ions increases with increasing pressure. We therefore conclude that the primary process involves the splitting of carbon bonds in a large fraction of ionizations. On this assumption, the curves of Figs. 4 and 5 should be horizontal straight lines. However, it has lately been pointed out by Kallman and Rosen[6] that insufficient attention has been given to selective absorption of ions in the ionization and magnetic deflection chambers of the positive ray tube. By experiments in which the pressures in the chambers were controlled separately, they were

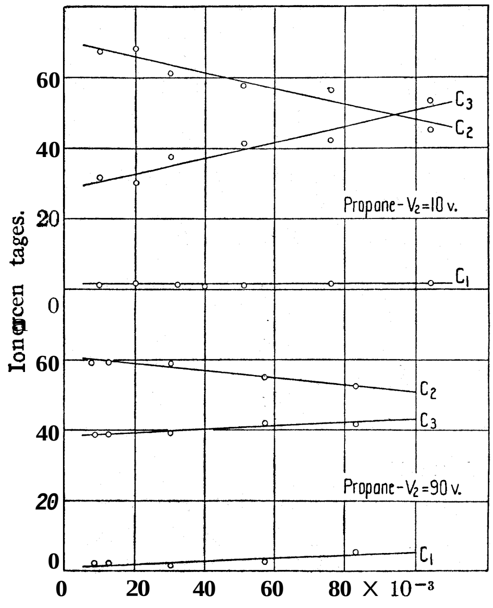

Fig. 4.—Ion percentage–pressure curves for propane. Ordinates represent percentages of total number of ions per second in a run in which the pressure in the ionization chamber is that given by the abscissa.

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[6] Kallman and Rosen, *Z. Physik*, 58, 52 (1929).

able to show in the case of nitrogen, previously an outstanding example of dissociation by secondary reaction alone, that all of the dissociation took place by primary electron impact, and that the observed variation in the percentages of N_2^+ and N^+ with pressure was due to strong selective absorption. It would be strange indeed if there were no similar effects for the hydrocarbons at the pressures employed. Thus the slopes of the ion percentage–pressure curves do not necessarily indicate secondary processes. This information, coupled with the fact that the percentage of the ion of the original hydrocarbon increases with pressure, and does not approach 100% as the pressure is reduced, definitely precludes any mechanism involving secondary reactions, at least for the principal effect.

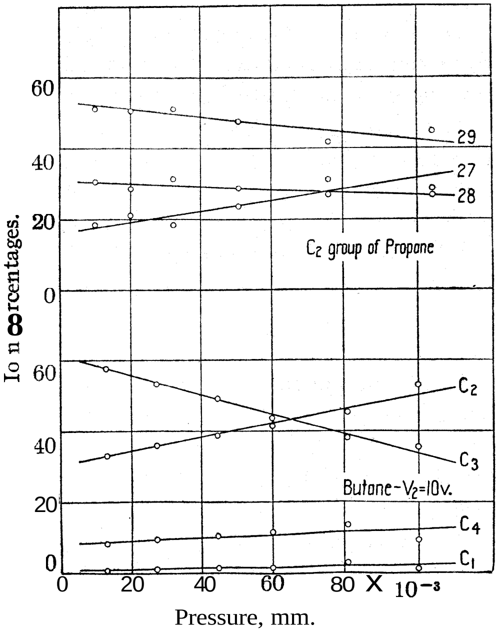

Fig. 5.—Ion percentage–pressure curves for butane and for the ions $C_2H_3^+$, $C_2H_4^+$ and $C_2H_5^+$ of the C_2 group in propane. Ordinates and abscissas are the same as in Fig. 4.

Simultaneous ionization and dissociation by electron impact can be explained satisfactorily by the same reasoning as was employed by Franck[6] for light absorption, and has been discussed in this light by Birge and Sponer[7] and others. As a result of electron impact, one electron may be removed from the hydrocarbon molecule, forming a positive molecule ion. It is also possible not only to remove an electron, but simultaneously to displace another electron to an excited level in which the binding force in a C–C or a C–H bond is weakened, and the equilibrium positions of the nuclei are more widely separated. If, then, as the result of an electron ejection, the equilibrium positions of the nuclei are suddenly at a greater distance apart than before, the two nuclei may, at the moment of ejection, be within the limiting distance of approach, and dissociation will follow.

Using propane as an example, the corresponding equations are

$$C_3H_8 \longrightarrow C_3H_8^+ + E^-$$
$$C_3H_8 \longrightarrow C_2H_5^+ + CH_3 + E^-$$
$$C_3H_8 \longrightarrow C_2H_5^+ + CH_3^+ + E^-$$
$$C_3H_8 \longrightarrow C_3H_7^+ + H + E^-$$

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[6] Franck, *Trans. Faraday Soc.*, *21,* 536 (1925).

[7] Birge and Sponer, *Phys. Rev.,* 28, 279 (1926).

The last equation also represents the fact that hydrogen ions were not observed in this work, and is similar to the one which Hogness and Kvalnes[3] found it necessary to assume in their study of methane.

To explain the multiple sub-peaks of propane and butane it seems necessary to assume that a single electron can eject a number of hydrogen atoms. This assumption is in accord with the work of Bleakney,[8] who has shown that a single electron can eject simultaneously as many as five electrons from mercury.

It may now be readily seen that the propane which Olson and Meyers reported had been formed from ethylene and hydrogen, may have been produced in the positive ray tube from the butane.

It is harder, as Taylor and Hill[9] point out, to understand why the positive ray analysis did not show the presence of methane in the ethane which had been exposed to ultraviolet light. The only explanation which we can offer is that the polymerization product of ethane deposited on the quartz window soon after beginning illumination and made the window opaque. Olson and Meyers[10] found that this was the case with ethylene.

Summary

1. By experiments with a specially designed tube, it is shown that the decomposition of the hydrocarbons in positive ray analysis is due to dissociation by the ionizing electrons, rather than to thermal decomposition by the hot cathode, or to secondary reaction between ions and neutral molecules.

2. It is shown that a previous determination of the saturated products of the hydrogen–ethylene reaction by positive ray methods gave ambiguous results, since part of the products reported have been found to decompose in the process of analysis.

3. Selective absorption of hydrocarbon ions by propane and butane is observed.

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[8] Bleakney, Phys. Rev., 34, 157 (1929).

[9] Taylor and Hill, THIS JOURNAL, 51, 2922 (1929).

[10] Olson and Meyers, *ibid.*, 48, 389 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SOUTH CAROLINA FOOD RESEARCH COMMISSION, AND THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF MINNESOTA MEDICAL SCHOOL]

THE DETERMINATION OF TRACES OF IODINE.
V. FURTHER REFINEMENTS IN TECHNIQUE

BY ROE E. REMINGTON, J. F. MCCLENDON AND HARRY VON KOLNITZ

RECEIVED DECEMBER 29, 1930 PUBLISHED APRIL 6, 1931

In previous papers of this series[1] there has been developed a technique for the micro-estimation of iodine in organic materials. Although the methods as described have been employed in a number of laboratories, further improvement seemed possible at certain points in the operation. It has been found practically impossible to avoid the formation of some tar or soot if organic matter is burned in the silica tube by the method described in the second and third papers, where the sources of heat were the heat of combustion of the material itself and a bank of Méker burners placed under the tube. The production of tar and soot necessitates a second burning, in a similar or smaller tube. Low temperature ignition in a muffle as previously described possesses the advantage of brevity, so essential in survey work where a large number of samples must be analyzed, and gives fairly accurate results on plant materials (except grain). Reith reports losses as high as 60% by this method when applied to flour or milk, but our results on milk powder have been quite as good as by any other method. It cannot be applied to nuts, cheese or other oily substances, which must be burned in the tube. Careful temperature control by automatic pyrometers is extremely necessary. In the fourth paper a small oxygen–gas torch was described, which insures sufficient heat to incinerate the sample thoroughly, and at the same time an excess of oxygen. Since this torch worked well on the small samples used in the determination of iodine in thyroid tissue, it seemed desirable to attempt to adapt it to reinforcing the heat of combustion of the larger samples necessary when foods or excreta are burned. Heat outside the silica tube as by Méker burners cannot be relied upon to maintain the stream of gases above the ignition point of organic combustion products, even though an excess of oxygen is always present. This external heat has therefore been replaced by a "hot spot" inside the tube over which the gases must pass, the hot spot consisting either of an electrically heated platinum spiral placed in a narrow part of the tube, or a roughly coiled piece of chromel wire placed a short distance in advance of the oxygen–gas torch. The platinum spiral has been found particularly adapted to the burning of such substances as urine and feces, which must be placed in combustion boats, while the flame-heated chromel wire has been found quite as satisfactory, and much simpler

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[1] McClendon and co-workers, THIS JOURNAL, 50, 1093 (1928); 51, 394 (1929); 52,541 (1930); 52,980 (1930).

in operation, for those substances which can be fed continuously, such as powdered dried vegetables by a screw feed device, or oils by an atomizer.

The flame-heated spiral inside the tube becomes very hot.[2] We have frequently been troubled with the appearance of nitrite in our absorbers, even when substances low or lacking in nitrogen, such as starch, were burned. This we have attributed to the fixation of atmospheric nitrogen, and have avoided by partially closing the opening around the screw feed device at the end of the tube, and so adjusting suction and oxygen supply that very little air is drawn in. Any appreciable amount of nitrite ruins the determination, since iodine is set free when the solution is acidified. The use of sodium sulfite instead of or in addition to hydroxide in the absorbers has been found desirable. Even so, it is a question whether all iodate is reduced by sulfite in alkaline solution, so that in some cases we have found it desirable to adopt the suggestion of Reith[3] to acidify and add sulfurous acid, and then make alkaline again before evaporation to complete dryness. Iodates are not extracted by alcohol. Reith also holds that alcohol will not make a complete extraction of iodides from a semi-crystalline mass, due to inclusion in the crystals. By making extraction in a ball mill, however, (which he did not do) and so adjusting our concentration of alcohol that a two-phase liquid system is formed, we are able to obtain satisfactory recoveries.

For burning any substances which can be continuously fed, such as oils by an atomizer or powdered substances by a screw-feed device, the set-up is essentially as previously described[4] except that the Méker burners are omitted, and the platinum spirals replaced by about 75 cm. of 20 gage chromel wire roughly coiled into a conical spiral and placed inside the silica tube about 5 cm. in advance of the point of delivery of the sample. To heat the spiral, two small copper tubes (1.5 mm. bore) are attached to the outside of the feed device, to deliver oxygen and gas. The ends of these tubes are brought together to form a torch immediately in front of the delivery point of the sample. The joint between the feed device and the silica tube is covered with a wad of wet asbestos, to exclude air as far as possible. The supply of oxygen is so adjusted as to furnish practically all the gas that is drawn through the absorbers. Burning is complete and extremely rapid, requiring only twenty minutes for 100 g. of material. A curved piece of 22 gage sheet nickel large enough to catch the ash, if inserted inside the silica tube, will facilitate removal of ash and lengthen the life of the tube. After the combustion, adhering particles of ash are

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[2] Platinum wire was tried for the spiral, but fused completely (m. p. 1755°). Tungsten wire (m. p. 3400°) was tried but ignited. The chromel wire becomes oxidized, but holds its form. Its life, however, is only one burning.

[3] J. F. Reith, *Biochem. Z.*, 224, 223 (1930).

[4] McClendon, Remington, von Kolnitz and Rufe, THIS JOURNAL, 52, 542, 544 (1930).

removed from the wire, which is preferably not placed in the solution, the tube and piece of nickel washed, washings combined with the solutions from the absorbers and the determination carried out as directed in previous papers. In burning oils, it is not practicable to feed both torch and atomizer from the same cylinder of oxygen. To check recovery when fats are burned by this method, we analyzed a sample of cod-liver oil, finding 10,400 parts of iodine per billion, and a sample of butter fat, finding 40 parts. The two were then mixed in proportions varying from 1 to 25 to 1 to 10, and burned. Percentage recoveries were, respectively, 80, 90, 80, 100, 91, 87, 84, 83, 82; average 86.

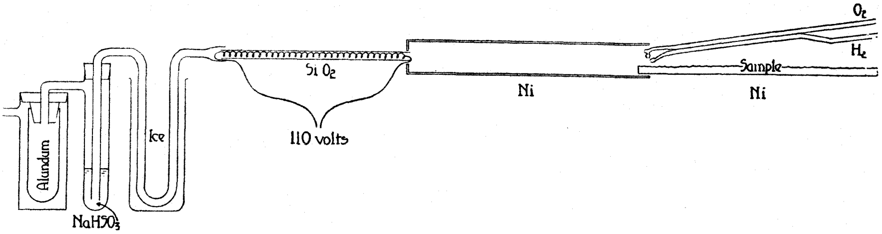

Fig. 1.

To burn urine residues and other pasty materials which cannot be packed into sausage casings nor sprayed, a different set-up has been devised (Fig. 1) This consists of a nickel tube of convenient diameter, into which a long nickel boat containing the sample is introduced. Nickel is used to reduce breakage when substances containing considerable amounts of fusible alkali, such as urine, are burned. The end of the nickel tube is constricted so as to fit over a silica tube of about 5 mm. bore, which contains a platinum spiral. This spiral is heated to a cherry red electrically by means of a 110-volt alternating current through an adjustable transformer. The joint between the nickel and silica tubes need not be perfectly tight but should be fitted fairly snugly. It is not necessary that the platinum wire be insulated from the nickel, but the whole apparatus can be placed on a dry wood or alberene table and the operator protected from accidental contact by wrapping the torch with tape. One end of the silica tube is introduced into the end of the U-shaped Pyrex tube, the joint being packed with wet asbestos. This tube is immersed in *a* beaker of cracked ice, and is connected with one or more Milligan wash bottles filled with sodium bisulfite solution. Finally the gases are drawn through an alundum capsule or Jena fritted glass filter to catch the white smoke which sometimes appears and is not absorbed by the wash solution. The nickel boat containing the sample is introduced gradually, the sample being burned by the small oxygen-gas torch shown in the drawing, which has a small opening in the oxygen supply tube, so placed as to allow a part of the oxygen to escape into the combustion tube above the sample. After the sample has all been introduced and burned, the torch is removed, the opening at the end is partly closed, oxygen being introduced continually, and the whole of the nickel tube is heated by means of a burner, so as to burn or volatilize any matter which may have been deposited in it during the earlier stage of the combustion. The washings from the apparatus and the liquid from the absorption vessels are combined and treated as previously described.

Pfeiffer[6] has developed an acid distillation method involving oxidation by perhydrol in sulfuric acid. We have tried the modification of this method proposed by Glimm and Isenbruch[6] but the operation is extremely time-consuming, is not adapted to large samples (in the tube furnace we have burned as high as 1 kg. of wheat or corn continuously), the oxidation is never complete, and the results are low in our hands. Out of more than twenty trials we were able to recover measurable quantities of iodine in only three. A sample of dried whey, which was the only one to give results comparable to the tube method, was carbonized in a dish before the acid digestion. A few typical results by these different methods are given in Table I.

TABLE I

SOME COMPARATIVE IODINE ESTIMATIONS BY DIFFERENT METHODS

Results are in parts per billion, dry basis

Sample	Source	Low temperature muffle		Acid distillation	Tube combustion	
Skim milk	Orangeburg, S. C.	371	354		316	
Skim milk	Newberry, S. C.	657			646	
Skim milk	Greenville, S. C.	840			862	
Skim milk	Edgefield, S. C.	169	166		314	
Skim milk	Greenwood, S. C.	1000			1300	
Whey	Greenwood, S. C.	1090	1070	1618	1768	1646
Cottonseed oil	Kershaw, S. C.				59	
Cottonseed meal	Kershaw, S. C.	111	104			
Cottonseed hulls	Kershaw, S. C.	111	117			
Oysters	McClellanville, S. C.			4,560	15,400	16,200
Osborne–Mendel salt mixture contg. citrates and a small amt. of iodide soln.				10,600	26,000 24,000	26,000

[a] Charred preliminary to acid digestion.

Turner[7] has recently described a method for estimating iodine in blood, in which he employs ashing in a current of oxygen in an open crucible, oxidation with bromine, the use of the iodide–iodate reaction, and colorimetric measurement of the blue color developed with starch. Although we have not worked on blood, we have repeatedly found that losses occur if ashing is done in open dishes at uncontrolled temperatures, even when an

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[5] G. Pfeiffer, ***Biochem. Z.***, 215, 126 (1929).

[6] E. Glimm and J. Isenbruch, *ibid.*, 207, 368 (1929).

[7] R. G. Turner, *J. Biol. Chem.*, 88,497 (1930); THIS JOURNAL, 52, 2768 (1930).

excess of alkali is used. Neither can we confirm his observations as to the reliability and stability of the color developed. If the blue solution is read against a blue glass instead of a starch–iodine solution, it will be found that the color is quite sensitive to temperature changes, and varies with time. Furthermore, in our hands, the depth of color produced by a given amount of iodine was not uniform. Four solutions, each prepared as described by Turner for his standard solutions, and each containing 0.001 mg. of I_2, read 22 5, 12.8, 9 24 and 26.0 mm. in the colorimeter, against our blue glass. Apparently there is some uncontrolled factor.

Other workers have made use of the iodide–iodate reaction to increase the iodine available for estimation. We have always felt that due to the uncertainty as to the presence of oxidizing substances other than iodate in extracts of the ash of plant and animal matter, and the effect of atmospheric oxygen on free hydriodic acid, this is a very dangerous procedure. It would be very desirable to increase the sensitivity of our present methods for substances such as blood or tissue, of which small amounts only are available, and for cereals or diets extremely low in iodine. Atmospheric effects can perhaps be eliminated by promptly removing the liberated iodine from the excess of potassium iodide by shaking out with carbon tetrachloride. This would move the lower limit of estimation down to about one-sixth its present value. When this was tried with pure solutions prepared by oxidation of known quantities of sodium iodide, the results were quite constant, and tended to approach the theoretical value, usually somewhat less. When, however, it was applied to extracts prepared from the ash of plant or animal matter, results were found to be extremely variable, and often many times the amount we had found to be present by other methods. Alcohol cannot be supposed to be an absolutely selective solvent for iodides to the exclusion of all other oxidizable substances.

Summary

1. An improvement in the destruction of organic matter in the micro-estimation of iodine by the tube furnace method, consists in a "hot spot" within the tube over which gaseous products must pass. This makes a second combustion unnecessary.

2. The perhydrol–sulfuric acid distillation method of Glimm and Isenbruch was found to be inapplicable to large samples of plant or animal matter, giving incomplete oxidation and low results.

3. The starch–iodide reaction is unreliable as a quantitative colorimetric method for estimation of iodine.

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THE DISSOCIATION CONSTANTS OF NITROGEN TETROXIDE AND OF NITROGEN TRIOXIDE

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RECEIVED JANUARY 8, 1931 PUBLISHED APRIL 6, 1931

It was found necessary to redetermine the dissociation constants of nitrogen tetroxide and nitrogen trioxide accurately as part of a larger program dealing with the kinetics of the decomposition of nitrogen pentoxide.

Although the dissociation of nitrogen tetroxide is used as a classical example of an equilibrium, the data are unsatisfactory and no attempts have been made to correct for deviations from the simple gas laws. In fact there has not been a sufficiently large number of independent measurements at any single temperature to determine quantitatively how these deviations affect the value of the dissociation constant and how it changes with pressure. Some of the earlier work was rendered inaccurate by the use of stopcock grease, rubber or mercury, but Bodenstein[1] in 1922 described accurate measurements using an all-glass apparatus at different temperatures. He gave two values of the equilibrium constant, one for high pressures and another for low pressures.

The dissociation constant of nitrogen trioxide had not been known with any accuracy and in fact the very existence of nitrogen trioxide in the gas phase was disputed. The earlier work was inaccurate because the apparatus was not chemically inert. Evidence that some nitrogen trioxide exists in a gaseous mixture of nitric oxide and nitrogen tetroxide is offered by the fact that when such a mixture is bubbled through alkali the oxides are absorbed in equivalent amounts to form almost pure nitrite; nitric oxide alone does not react and nitrogen dioxide gives equal quantities of nitrite and nitrate. Wourtzel[2] obtained two good measurements of the equilibrium constant by allowing nitric oxide to mix with an insufficient supply of oxygen. After the work described in this communication was well started a preliminary article on nitrogen trioxide was published by Abel and Proisl.[3] Although the apparatus and technique was similar to that of the present authors, the work was not discontinued because it seemed desirable to have measurements of such an uncertain quantity from two different laboratories.

Furthermore, it seemed likely that accurate measurements on these two equilibria might reveal the possible existence of oxides of nitrogen other than the four in question. Such oxides would be of interest in connection with studies on kinetics. To determine the effect of inert gases

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[1] Bodenstein, Z. *physik. Chem.*, **100**, 68 (1922).

[2] Wourtzel, *Compt. rend.*, **170**, 109 (1920).

[3] Abel and Proisl, Z. *Electrochem.*, **35**, 712 (1929).

on the equilibrium and the rate of dissociation, measurements were made in the presence of such gases.

Experimental Procedure

The apparatus is shown in Fig. 1. It is so constructed that the reacting gases come in contact with no material other than glass. Each gas is sealed off in a one-liter Pyrex flask and its pressure is measured by means of the glass manometer developed in this Laboratory.[4] A measured air pressure is balanced against the pressure in the flask through a glass diaphragm which is provided with an electrical contact. The air can be evacuated rapidly through K or slowly through the capillary J or the pressure may be allowed to increase rapidly through H or slowly through G, thus facilitating the rapid and exact adjustment of the balancing pressure. Calcium chloride tubes are used to keep the manometer system dry. A trap L and an automatic check valve N, consisting of a glass bead seated on a small rubber tube inside a glass tube, were used to prevent water running back from the aspirator.

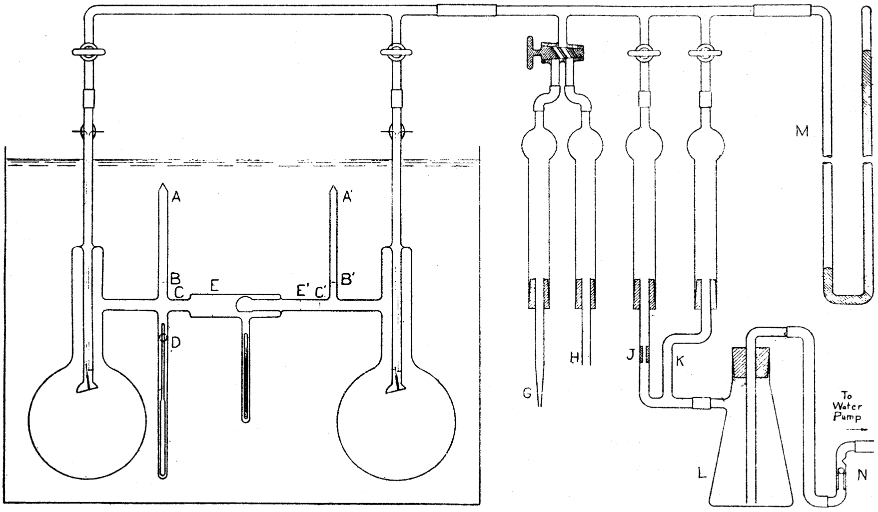

Fig. 1.

The device for keeping the gases separate and later allowing them to mix consists of a glass bulb blown from 12-mm. tubing and flattened on one side; this is sealed into 20-mm. tubing, and a side tube attached opposite the flat place. This central piece is now sealed onto the side arms of the two flasks at E and E', and the flasks clamped in position on the ring stand which is later to be set into the thermostat. An iron nail enclosed in glass tubing of such a size that it moves easily inside the side tube is now inserted in the latter and the tube sealed off so as to leave about two centimeters in which the hammer may move. When it is desired to break the bulb, a solenoid is placed around the side tube and the hammer driven up into the bulb when a current is sent through the solenoid. It is imperative that the bulb be flattened; the keystone effect of a spherical bulb is so marked that the glass of the hammer breaks instead of the bulb. The most durable hammers are those made of soft glass padded with asbestos at each end of the nail. The asbestos serves to keep the iron from scratching the glass and to equalize the pres-

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[4] Daniels, THIS JOURNAL, 50,1115 (1928)

sure of the nail on the end of the tube as it is bumped against the bulb. The glass must be worked quickly in the flame and at some distance from the nail, to prevent the temperature strains which would result if the metal were allowed to become heated. In these experiments, small finishing nails ground round on the ends and sealed inside four millimeter tubing moving in seven millimeter tubing, were used as hammers.

The solenoid was made by winding 400 ft. of No. 24 double cotton covered copper wire on a brass tube about **6** cm. long. It was connected in series with a rheostat to a **55** v. direct current circuit and operated at a current of five amperes or less.

A similar device was used at D for breaking the file-scratched capillary of a bulb containing nitrogen tetroxide.

The volumes of the flasks were obtained by filling with distilled water to marks at B, C and B', C' and weighing. After the center piece was inserted, the volumes on each side of the bulb were obtained by tipping to one side or the other and running in water from a standardized buret through A and A' to C and C'.

The outside volume of the filled nitrogen tetroxide bulb was found from the volume of water displaced by it and the inner volume of the broken bulb was determined after the completion of an experiment by running in water from a buret. The difference between the two gives the volume of glass in the bulb. The volumes of the side arms A and A' were obtained at the end of the run by inverting the flasks and filling the arms to the marks B and B' from a buret.

A second apparatus using 500-cc. flasks connected by 20-mm. tubing was also used. No difference could be detected in the results obtained with the different apparatus. The larger connecting tube decreased the time necessary for complete diffusion of the two gases.

The gas for the right-hand flask was prepared and stored over concentrated sulfuric acid in a two-liter flask with a three-way stopcock. When the gas was needed, the stopcock was sealed to the filling tube A'. The inorganic stopcock lubricant described by Stephens[6] was used. It was prepared by heating a mixture of 85% phosphoric acid and metaphosphoric acid to 300°.

The two flasks of known volume are sealed to the center piece and the whole clamped in position. After setting in the hammer, the flasks are dried and evacuated thoroughly and the zero points of the diaphragms are determined. A bulb of known volume containing a weighed amount of nitrogen tetroxide is dropped in through A and the left-hand flask evacuated thoroughly while being heated with a luminous flame to drive out adsorbed water. It is then sealed off at A and the side arm A' is sealed to the gas holder and evacuated through the three-way stopcock, while the flask is heated. Some gas is allowed to enter the flask and then it is re-evacuated; finally it is filled with gas to approximately the desired pressure and sealed off. The nitrogen tetroxide bulb is broken, the apparatus immersed in the thermostat, and the pressure in the two flasks determined. The separating bulb is then broken and the pressures determined at intervals until there is no further change, showing that diffusion has been complete and equilibrium has been reached. The flasks are next opened to the atmosphere and the zero points re-determined. The broken center piece is cut off at E and E' and the volumes of the arms A and A' and of the nitrogen tetroxide bulb determined. After sealing in a new central piece the apparatus is ready for a second determination.

The apparatus was completely immersed in a large water thermostat the temperature of which was kept constant to within 0.05" and measured with a calibrated thermometer. The closed-end manometer agreed with a standard barometer within 0.2 mm. and the glass diaphragm gave readings reproducible to within 1 mm. All manometer readings were corrected to 0°.

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[6] Stephens, THIS JOURNAL, 57,635 (1930).

The nitrogen tetroxide was prepared by heating lead nitrate and condensing the gas in a flask containing phosphorus pentoxide, from which it was redistilled after several days into weighed bulbs, in the manner described by Daniels, Mathews and Williams.[6]

There was some possibility that this method of procedure might allow the nitrogen tetroxide to become contaminated with moisture, due to diffusion of air down the tube while being filled. To eliminate this uncertainty, several experiments were made with nitrogen tetroxide sealed off in the following manner. A tube of the shape shown in Fig. 2 was weighed, and the bulb *Q* filled with phosphorus pentoxide. Nitrogen tetroxide was now distilled into the bulb and the tube sealed off at R. The nitrogen tetroxide was allowed to dry for a few days and then distilled over into the right-hand arm, which was then sealed off at S. All the glass was then thoroughly cleaned and dried, and reweighed; the difference between the original and final weights gave the weight of nitrogen tetroxide sealed in the bulb. Experiments using this technique gave results in agreement with those of the simpler technique described in the reference, whence the conclusion was drawn that the simpler procedure was satisfactory.

Nitric oxide was prepared from sodium nitrite and sulfuric acid according to Noyes,[7] bubbled through sulfuric acid and stored over concentrated sulfuric acid in the gas holder.

Measurements of $N_2O_4 \rightleftarrows 2NO_2$.—In every experiment of this investigation liquid nitrogen tetroxide was weighed out and the pressure and volume of the gas were measured in the left-hand flask. In several experiments the right-hand flask was evacuated and a second determination of the dissociation constant was made at a lower pressure after breaking the connecting bulb.

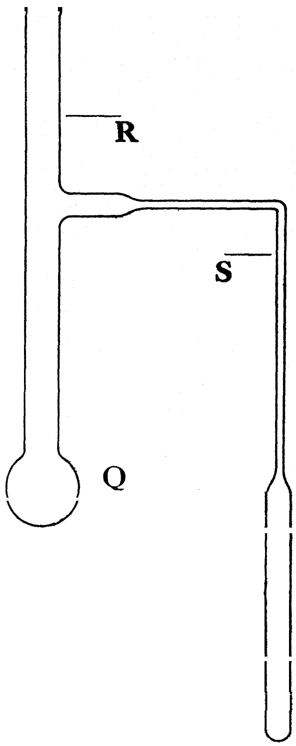

Fig. 2.

In all cases the dissociation constant, $K_{N_2O_4}$, was calculated from the formula

$$K_{N_2O_4} = \frac{4\alpha^2 P}{1 - \alpha^2}$$

where P is the measured pressure in atmospheres and α is the degree of dissociation as defined by the expression

$$\alpha = \frac{P - p^0_{N_2O_4}}{p^0_{N_2O_4}}$$

$p^0_{N_2O_4}$ is the pressure which would be exerted by undissociated nitrogen tetroxide, *i. e.*

$$p^0_{N_2O_4} = \frac{g}{M}\frac{RT}{V}$$

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[6] Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1929, p. 115.

[7] W. A. Noyes, This Journal, 47, 2170 (1925).

in which g is the weight of nitrogen tetroxide, *M* is the molecular weight, and R, T and V have their usual significance.

In these and all subsequent calculations a lower case *p* with subscript referring to the gas in question indicates the partial pressure of that gas; a superscript zero indicates the idealized pressure which the gas would exert if it did not dissociate nor react with other gases; and a capital P represents the total, measured pressure.

TABLE I

EQUILIBRIUM $N_2O_4 \rightleftarrows 2NO_2$ AT 25.0°

$C^0_{N_2O_4}$, *moles* N_2O_4/liter $\times 10^3$	*P*, *atm.*	$K_{N_2O_4}$	$C^0_{N_2O_4}$, *moles* N_2O_4/liter $\times 10^3$	*P*, *atm.*	$K_{N_2O_4}$
4.49	0.1566	0.1380	14.18	0.4369	0.1265*
6.28	.2118	.1419*	14.93	.4588	.1294
6.51	.2172	.1323	14.98	.4598	.1278
7.65	.5129	.1384†	15.39	.4743	.1381
8.90	.2889	.1378	15.85	.4843	.1290*
8.98	.6543	.1325‡	16.67	.5107	.1393
9.33	.5699	.1359†	17.31	.5254	.1295
9.87	.3150	.1287*	18.01	.5435	.1261
10.15	.3271	.1470*	18.02	.5443	.1274
10.54	.3357	.1349	18.40	.5554	.1290
11.62	.3660	.1318*	18.99	.5719	.1292
12.10	.3793	.1310	19.84	5996	.1412*
12.26	.3841	.1318*	20.07	.6007	.1272
12.59	.3941	.1340*	20.90	.6214	.1218
12.59	.3942	.1340*	21.40	.6349	.1205
12.89	.4021	.1319	21.62	.6373	.1121
13.59	.4213	.1303	27.72	.8081	.1236
			29.68	.8623	.1261*

TABLE II

EQUILIBRIUM $N_2O_4 \rightleftarrows 2NO_2$

$C^0_{N_2O_4}$, moles/liter $\times 10^3$	35.0°			45 0°		
	P, *atm.*	$K_{N_2O_4}$	AH (25–35°)	*P*, *atm.*	$K_{N_2O_4}$	Δ*H* (35–45°)
6.28	0.2382	0.3174	14700	0.2662	0.6771	14760
9.87	.3533	.2950	15140			
10.15	.3649	.3163	13990	,4064	.6491	14010
11.62	.4086	.2937	14640	4554	.6103	14250
12.26	.4287	.2953	14730			
12.59	.4391	,2949	14400	.4889	.6104	14180
12.59	.4400	,3007	14670	.4903	.6266	14320
14.18	.4871	.2877	15010	.5446	.6230	15050
15.85	.5378	.2859	14540	.5985	.5993	14420
16.67	.5659	.3016	14110	.6295	.6290	14340
17.31	.5823	.2860	14470	.6484	.6068	14660
19.84	.6623	.3032	13950	.7349	.6280	14190
21.62	.7065	.2644	15670	.7834	.5567	14510
27.72	.8902	.2806	14950	.9814	.5718	13850
29.68	.9470	.2792	14520	1.0474	.5934	14700

The experimental results are summarized in Tables I and II and in Fig. **3.** In each case the ideal concentration, $C^0_{N_2O_4}$, is given assuming no dissociation. In Table I the values marked (*) were determined with the special drying precautions described above. The two marked (†) were obtained in the presence of 0.2608 and 0.2689 atmosphere of oxygen and the experiment marked ($) was made in the presence of 0.3643 atmosphere of carbon dioxide. These determinations are designated with triangles in Fig. **3.** In these experiments the right-hand flask was filled with the foreign gas before breaking the connecting bulb.

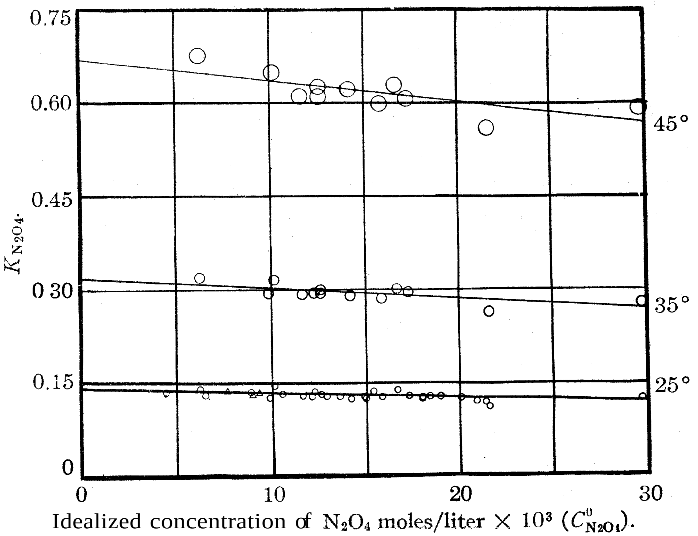

Fig. 3.

The calculation of the dissociation constant is such that an error of 1 mm. in the pressure measurements introduces a larger error in the value of the equilibrium constant at 45° than at 25° and the circles have been drawn larger. In each case the radius is a measure of the experimental accuracy.

The heat of dissociation, ΔH, as calculated from the van't Hoff equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H\ (T_2 - T_1)}{2.303\ R\ T_2T_1}$$

is included for each experiment in Table II. Although the equilibrium constant is markedly affected at the higher pressures by the deviations from the perfect gas laws, the heat of dissociation remains nearly constant.

Measurements of $N_2O_3 \rightleftarrows NO_2 + NO$.—When nitrogen tetroxide expands into an evacuated space the resulting pressure is greater than that calculated by the ideal gas laws on account of the greater dissociation into nitrogen dioxide at the lower pressures. When it expands into an inert gas the partial pressures of nitrogen tetroxide and nitrogen dioxide are still the same as when expanding into an evacuated space, but when it expands into nitric oxide the pressures are smaller on account of the reaction

$$NO_2 + NO \rightleftharpoons N_2O_3$$

The calculation of the equilibrium constant for this reaction is complicated by the fact that as soon as nitrogen dioxide is used up more nitrogen tetroxide dissociates. However, the following relations between the partial pressures of the gases present must hold under any conditions

$$\begin{aligned} K_{N_2O_4} &= p_{NO_2}{}^2/p_{N_2O_4} \\ p^0_{NO} &= p_{NO} + p_{N_2O_3} \\ 2p^0_{N_2O_4} &= 2p_{N_2O_4} + p_{NO_2} + p_{N_2O_3} \\ P &= p_{N_2O_4} + p_{NO_2} + p_{NO} + p_{N_2O_3} \end{aligned}$$

At equilibrium, these four equations must be simultaneously satisfied. The four values on the left are experimentally measured quantities. $K_{N_2O_4}$ is the value of the equilibrium constant for the reaction

$$N_2O_4 \rightleftharpoons 2NO_2$$

obtained from the curves in Fig. **3** for the particular concentration of nitrogen tetroxide existing in the final volume, as calculated from the original weight of nitrogen tetroxide. **A** very slight approximation is being made here, because the concentration of nitrogen tetroxide will decrease on account of the formation of some nitrogen trioxide; the resulting change in K, however, will cause no change in the results within the experimental error. p^0_{NO} is the pressure which would be exerted by the original quantity of nitric oxide if present alone in the final volume. $p^0_{N_2O_4}$ is the pressure exerted by the original weight of nitrogen tetroxide if present alone and undissociated in the final volume. **P** is the total pressure as measured at the end of the experiment.

Solving these four equations simultaneously

$$\begin{aligned} p_{NO_2} &= \frac{-K_{N_2O_4} + \sqrt{K^2_{N_2O_4} + 4K_{N_2O_4}(P - p^0_{NO})}}{2} \\ p_{NO} &= 2P - p^0_{N_2O_4} - p^0_{NO} - p_{NO_2} \\ p_{N_2O_3} &= p^0_{NO} - p_{NO} \end{aligned}$$

whence $K_{N_2O_3}$ can be calculated from

$$K_{N_2O_3} = \frac{p_{NO} \times p_{NO_2}}{p_{N_2O_3}}$$

The results are shown in Tables III, IV and V and in Fig. 4, in which the values of $K_{N_2O_3}$ are plotted against the concentration of nitrogen trioxide assuming no dissociation; that is against $C^0_{N_2O_3}$ where

$$C^0_{N_2O_3} = 1/2(p_{NO_2} + p_{NO} + 2p_{N_2O_3})\,\frac{1}{RT}$$

In the determination of $K_{N_2O_3}$ there is a large accumulation of errors such that the experimental error amounts to about 10%. The curves for the three different temperatures are plotted on different scales, such that the radius of the circles drawn around the points represents in each case the experimental error.

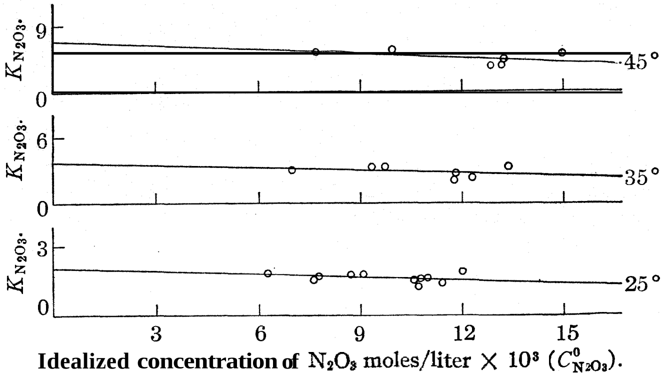

Fig. 4.

The data and calculations for the first experiment in Table III are given to illustrate the details of the method. Here the weight of nitrogen

Table III

Equilibrium $N_2O_3 \rightleftarrows NO + NO_2$ at 25°

$C^0_{N_2O_4} \times 10^3$	p^0_{NO}	P	$C^0_{N_2O_3} \times 10^3$	$K_{N_2O_3}$
6.24	0.1834	0.3868	6.26	1.87
6.76	.2397	.4551	7.62	1.59
8.96	.2246	.5046	7.76	1.74
5.77	.3048	.4902	8.72	1.83
6.12	.3177	.5131	9.09	1.86
9.45	.3477	.6346	10.58	1.54
11.03	.3351	.6638	10.71	1.28
14.15	.3057	.7261	10.77	1.63
9.99	.3614	.6631	10.98	1.59
8.58	.3955	.6540	11.44	1.42
15.18	.3736	.8205	12.02	1.98

Table IV

Equilibrium $N_2O_3 \rightleftarrows NO + NO_2$ at 35°

$C^0_{N_2O_4} \times 10^3$	p^0_{NO}	P	$C^0_{N_2O_3} \times 10^3$	$K_{N_2O_3}$
6.24	0.1900	0.4199	6.99	2.99
5.77	.3144	.5257	9.34	3.26
6.12	.3287	.5509	9.74	3.26
11.03	.3466	.7173	11.77	2.09
14.15	.3160	.7868	11.82	2.65
8.58	.4093	.7027	12.32	2.30
15.18	.3862	.8866	13.43	3.26

TABLE V

EQUILIBRIUM $N_2O_3 \rightleftharpoons NO + NO_2$ AT 45°

$C^0_{N_2O_4} \times 10^3$	p^0_{NO}	P	$C^0_{N_2O_3} \times 10^3$	$K_{N_2O_3}$
6.24	0.1958	0.4544	7.69	5.36
5.77	.3243	.5625	9.97	5.66
11.03	.3576	.7753	12.89	3.38
8.58	.4226	.7530	13.23	3.46
14.15	.3263	.8540	13.25	4.22
15.18	.3989	.9605	14.98	5.07

tetroxide introduced into the left-hand flask was 1.2798 g., the volume of the flask was 1.1042 liters, the pressure, P, at 25°, 299.6 mm. From these data, $K_{N_2O_4}$ is calculated.

$$p^0_{N_2O_4} = \frac{1.2798 \times 0.08206 \times 298}{92.02 \times 1.1042} = 0.3080$$

$$\alpha^2 = \left(\frac{P - p^0_{N_2O_4}}{p^0_{N_2O_4}}\right)^2 = \left(\frac{\frac{299.6}{760} - 0.3080}{0.3080}\right)^2 = 0.0783$$

$$K_{N_2O_4} = \frac{4\alpha^2}{1 - \alpha^2}P = \frac{4 \times 0.0783}{0.9217} \times 0.3942 = 0.1340$$

$$C^0_{N_2O_4} = \frac{1.2798}{92.02 \times 1.1042} = 12.59 \times 10^{-3}$$

The volume of the right-hand flask was 1.1254 liters and the pressure of nitric oxide in it was 276.2 mm. The final pressure measured at equilibrium after breaking the connection was 294.0 mm. From these data and those above, $K_{N_2O_3}$ is calculated as follows.

$$p^0_{NO} = \frac{276.2}{760} \times \frac{1.1254}{(1.1254 + 1.1042)} = 0.1834$$

$$C^0_{N_2O_4} = \frac{1.2798}{92.02 \times 2.2296} = 6.236 \times 10^{-3}$$

From an equation given below for the curve in Fig. 3

$$K_{N_2O_4} = 0.1426 - 0.7588 \times 6.236 \times 10^{-3} = 0.1379$$

$$p^0_{N_2O_4} = \frac{1.2798}{92.02} \times \frac{0.08206 \times 298}{2.2296} = 0.1525$$

$$P = \frac{294.0}{760} = 0.3868$$

These values for $p^0_{N_2O_4}$, p^0_{NO}, P, and $K_{N_2O_4}$ are to be substituted in the solutions of the simultaneous equations already given, to give

$$p_{NO_2} = \frac{-0.1379 + \sqrt{(0.1379)^2 + 4 \times 0.1379(0.3868 - 0.1834)}}{2} = 0.1122$$

$$p_{NO} = 2 \times 0.3868 - (2 \times 0.1525 + 0.1834 + 0.1122) = 0.1730$$

$$p_{N_2O_3} = 0.1834 - 0.1730 = 0.0104$$

$$K_{N_2O_3} = \frac{0.1122 \times 0.1730}{0.0104} = 1.87$$

$$C^0_{N_2O_3} = 1/2(0.1122 + 0.1730 + 2 \times 0.0104)\frac{1}{0.08206 \times 298} = 6.27 \times 10^{-3}$$

Discussion

The number of independent measurements at a single temperature is sufficiently great to permit reliable calculations of the influence of pressure on the equilibrium constants. The three curves of Fig. 3 are reproduced by the following equations obtained by the method of least squares.

TABLE VI

$N_2O_4 \rightleftharpoons 2NO_2$

Temp, °C.	Equilibrium constants ($C^0_{N_2O_4}$ = total weight/92 02 X volume in liters)
25	$K_p = 0.1426 - 0.7588 \times C^0_{N_2O_4}$
35	$K_p = .3183 - 1.591 \times C^0_{N_2O_4}$
45	$K_p = .6706 - 3.382 \times C^0_{N_2O_4}$

The idealized equilibrium constants extrapolated to zero pressure are 0.1426 at 25°, 0.3183 at 35° and 0.6706 at 45°. These values are important for they give the equilibrium constants for perfect gases and the laws of thermodynamics may be applied with exactness. They correspond to values obtained with fugacities or activities rather than pressures. Then

$$-\mathrm{AF}^{\circ} = RT \ln K_p$$

and $\Delta F^{\circ}_{298} = 1154$ calories, $\Delta F^{\circ}_{308} = 700$ calories and $\Delta F^{\circ}_{318} = 252$ calories. AF° is the increase in free energy necessary to convert one mole of nitrogen tetroxide at a fugacity of 1 atmosphere into 2 moles of nitrogen dioxide at a fugacity of 1 atmosphere. From the free energy of formation of nitrogen dioxide[8] the free energy of formation of 1 mole of nitrogen tetroxide from nitrogen and oxygen at 25° and 1 atmosphere is 23,836 calories.

The heat of dissociation, *AH*, calculated from the values of the equilibrium constant extrapolated to zero pressure gives from 25–35° 14,670 cal., from 35–45" 14,530 cal. The entropy change, *AS*, may be calculated from the equation

$$AF = \mathrm{AH} - T\Delta S$$

using the average value of the heat of dissociation AH = 14,600. *AS* is constant over this range of temperature and equal to 45.1 entropy units.

The values of the equilibrium constant are somewhat lower than those calculated for corresponding pressures from the equations of Bodenstein.[1]

By weighing out the samples of nitrogen tetroxide, a more direct evaluation of the amount of material present is obtained than by the method of Bodenstein, who determined the concentration of nitrogen dioxide from the pressures existing at temperatures in the neighborhood of 150°, making corrections for the nitrogen tetroxide and nitric oxide and oxygen present at those temperatures. Further, this communication reports a large number of separate determinations made on different samples of

[8] "International Critical Tables" ("revised" data of Randall and White), McGraw-Hill Book Co., Inc., New York, Vol. VII, 1930, p. 239.

tetroxide, whereas Bodenstein used one original sample and obtained results at lower pressures by progressively removing portions of this original material from the reaction flask. On the other hand, Bodenstein's manometer was more sensitive and the temperature range studied was considerably greater.

The decrease in the equilibrium constant with increase in pressure is due to the deviation of the gases from the ideal gas laws. Although the critical data for the gases are inaccessible to experimental measurement, it is reasonable to assume that they are similar to those of sulfur dioxide, which has a structure somewhat like that of nitrogen dioxide and a boiling point near that of nitrogen tetroxide. Assuming that the mixture of gases in the reaction vessel acts like sulfur dioxide, as far as its non-ideal properties are concerned, it is possible to idealize the total pressure and recalculate α and $K_{N_2O_4}$. Using Berthelot's equation of state and the critical data of sulfur dioxide ($T_c = 430°K.$ and $P_c = 78$ atm.), the values of $K_{N_2O_4}$ calculated from the idealized pressures agree with those obtained by extrapolating to zero pressure.[9]

In spite of the fact that the change of K with pressure seems to be explained by the deviation of nitrogen tetroxide and nitrogen dioxide from the gas laws, there was a further possibility that it might be due to increased adsorption of the gases on the glass walls at higher pressures, complicated by a preferential adsorption of the nitrogen tetroxide over the nitrogen dioxide. From the start it seemed unlikely that the decrease of K could be explained in this way, because calculation showed that at a concentration of 0.030 mole/liter, the unlikely amount of 0.037 g. of material would have to be adsorbed in the liter flask at 25° in order to account for the drop from K = 0.1426 at zero concentration to K = 0.1198 at a concentration of 0.030 mole/liter. To investigate this point, scales of Pyrex glass made by breaking up thin bulbs, with a total surface at least twice as great as the inner surface of a flask, were put into a U-tube, covered with water overnight in order partially to etch the surface, dried by heating in a stream of dry air, and then weighed. Liquid nitrogen tetroxide was poured into the tube, the liquid allowed to evaporate and the U-tube re-weighed. An increase in weight of only 0.0013 g. was observed. In another experiment, gaseous nitrogen tetroxide was passed through the weighed U-tube; no increase in weight could be detected.

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[9] The fact that one constituent of the gas mixture may show a deviation from the gas laws different in degree from that of the other does not alter this result. Any idealization whatsoever must increase the total pressure and, consequently, the degree of dissociation; the equilibrium constant is thus increased in every case, in spite of the fact that, as is probably true, a greater correction is to be applied to nitrogen tetroxide than to nitrogen dioxide. The assumption made above is that the combined effect of the deviations of the two gases is such as to give a resultant non-ideality, over the temperature range in consideration, like that of sulfur dioxide.

Finally, glass scales having an area over twenty times as great as that of the inner surface of a liter flask, were treated overnight with chromic acid, washed and dried. A regular determination of the equilibrium constant with this extra glass in the apparatus showed that any adsorption of nitrogen tetroxide or nitrogen dioxide is entirely negligible.

The fact that inert gases such as oxygen and carbon dioxide do not affect the equilibrium constant is of interest in kinetics. The decomposition of nitrogen tetroxide is probably unimolecular and its formation is a bimolecular reaction. If a large increase in the number of collisions affects either reaction more than the other, the equilibrium constant should be shifted. However, no influence of this kind was found.

An interesting observation regarding diffusion was made during the course of the experiments. When the nitrogen tetroxide'in the left-hand flask was allowed to expand into a vacuum the equilibrium was reached quickly. When the right-hand flask was filled with a gas, such as oxygen, carbon dioxide or nitric oxide, twenty hours or more were necessary to insure complete mixing of the gases. The rate of diffusion was determined qualitatively by observing the decrease in red color in the left-hand flask and its increase in the right-hand flask. It was measured more quantitatively by observing the pressure increase on standing. As the nitrogen tetroxide diffuses to regions of lower concentrations it dissociates to a greater extent and increases the total pressure. In many experiments involving the mixing of gases there is no simple indicator to tell when the mixing is complete. With a smaller connecting tube or with a stopcock in the tube, the rate of mixing would be very much lower.

The curves of Fig. 4 are reproduced by the following equations obtained by the method of least squares.

TABLE VII

$N_2O_3 \rightleftharpoons NO_2 + NO$

Temp., °C.	Equilibrium constants
25	$K_p = 2.105 - 45.63\ C^0_{N_2O_3}$
35	$K_p = 3.673 - 78.11\ C^0_{N_2O_3}$
45	$K_p = 6.880 - 196.4\ C^0_{N_2O_3}$

The heat of dissociation calculated from the van't Hoff equation between 25 and 35" is 10,160 at zero concentration (from extrapolated values of K) and 10,310 at a concentration of 15 X 10^{-3} moles per liter. Calculating between 35 and 45" the heat of dissociation is 12,210 at zero concentration and 8820 at a concentration of 15 × 10^{-3}. From the constancy of the value of $\Delta H_{(25-35°)}$ as the pressure changes and from analogy with the results on nitrogen tetroxide, it seems likely that the variation of $\Delta H_{(35-45°)}$ is due to experimental error. At 45° the errors are considerably magnified and the number of determinations is rather small.

The curve is probably slightly too steep. An average of the four values gives A H = 10,300.

The free energies changes are as follows:

$$\Delta F^\circ_{298} = -441 \qquad \Delta F^\circ_{308} = -796 \qquad \Delta F^\circ_{218} = -1218$$

and using the data of "International Critical Tables," Vol. VII, p. 238, for the free energy of formation of nitric oxide and nitrogen dioxide, the free energy of formation of nitrogen trioxide from its elements is 33,805 calories.

The values of the equilibrium constant check only fairly well with those of Abel and Proisl.[3] For example, at 25° the value of K extrapolated to zero concentration from their curve and translated into the notation used in this communication gives 1.43 as against the value of 2.10 given here.

The straight line relation between $C_{N_2O_3}$ and $K_{N_2O_3}$ seems definitely to indicate that this reaction is actually

$$NO + NO_2 \rightleftarrows N_2O_3$$

No other reaction gives a smooth straight line. If the equilibrium constant is calculated from

$$2NO + 2NO_2 \rightleftarrows N_4O_6$$

the "constant" varies greatly with pressure, even though fairly regularly. If the reaction is considered to be

$$N_2O_4 + 2NO \rightleftarrows 2N_2O_3$$

the equilibrium "constant" shows wide and irregular variations. If the calculations are made from

$$N_2O_4 + 2NO \qquad N_4O_6$$

the "constant" is very irregular.

It is believed that the results of the present investigation show that the dissociation of nitrogen tetroxide is correctly represented by the equation $N_2O_4 \rightleftarrows 2NO_2$ and that the dissociation of nitrogen trioxide is correctly represented by the equation $N_2O_3 \qquad NO + NO_2$. Within the limits of experimental accuracy recorded here it may be concluded that no other oxides of nitrogen are present in appreciable amounts in the partially dissociated gases.

Summary

1. The dissociation constant for gaseous nitrogen tetroxide has been measured at 25, 35 and 45° with special reference to the influence of pressure. The dissociation constant is directly proportional to the pressure and is about 13% greater at 0.1 atmosphere than at 1 atmosphere.

2. The presence of inert gases such as oxygen and carbon dioxide has no effect upon the dissociation constant in the above reaction.

3. The dissociation constant for gaseous nitrogen trioxide has been measured with an all-glass apparatus at 25, 35 and 45° at different pressures.

4. The value of the equilibrium constant is not affected by any adsorption on the glass walls.

5. The influence of pressure on the equilibrium constants can be attributed to deviations from the simple gas laws.

6. The true equilibrium constants for thermodynamical calculations have been determined by extrapolation to zero pressure. Calculations are given for ΔF, ΔH and ΔS.

7. The measurements indicate that the dissociations proceed according to the reactions $N_2O_4 \rightleftharpoons 2NO_2$ and $N_2O_3 \rightleftharpoons NO + NO_2$.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE, ENGLAND]

THE DIELECTRIC PROPERTIES OF ANTIMONY PENTACHLORIDE AND PHOSPHORUS PENTACHLORIDE[1]

BY J. H. SIMONS AND GILBERT JESSOP

RECEIVED JANUARY 14, 1931 PUBLISHED APRIL 6, 1931

The dielectric properties of antimony pentachloride and phosphorus pentachloride were studied in the hope of adding some information on which to consider the structure of these compounds.

The apparatus used has been described by Lowry and Jessop.[2] The materials used were carefully purified. The carbon tetrachloride was treated with chlorine and allowed to stand in sunlight for several days. It was dried with freshly fused calcium chloride and distilled. The antimony pentachloride was distilled three times in a vacuum and kept sealed in glass. It had a very light color and a sharp melting point. The phosphorus pentachloride used to make the solutions was contained in a small sealed glass vessel into which it had been distilled in vacuum.

In order to test out the apparatus, the dielectric constant of pure dry carbon tetrachloride was determined in it over a range of temperatures. These values and also the molar polarizations calculated from them are given in Table I. These agree very well with published data.[3] Pure benzene and chloroform were used to calibrate the cell. The densities

TABLE I

DIELECTRIC CONSTANT AND MOLAR POLARIZATION OF CARBON TETRACHLORIDE

Temp., °C.	Dielectric constant	Density, g./cc.	Molar polarization. cc.
3.5	2.268	1.62638	28.1
16.5	2.239	1.60128	28.1
26.3	2.217	1.58230	28.0
46.4	2.171	1,54264	28.0

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[1] Part of this work was done during the time that one of the authors, J. H. Simons, was a National Research Council Fellow.

[2] Lowry and Jessop, J. Chem. *Soc.*, 782 (1930).

[3] Compare Stranathan, *Phys. Rev.*, 31, 653 (1928).

were determined with calibrated quartz floats by the method described by Lowry and Jessop.[4]

The Molar Polarization of Antimony Pentachloride and Phosphorus Pentachloride in Solution in Carbon Tetrachloride.—The density and capacity of these solutions were determined over a range of temperatures. The results are given in Tables II and III together with the molar polarizations calculated from them by means of the modified Clausius and Mosotti eauation[6]

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{M_1f_1 + M_2f_2}{\rho} = P_1f_1 + P_2f_2$$

As the molar polarizations of both antimony pentachloride and phosphorus pentachloride show no appreciable deviation with temperature, it can be assumed that if these molecules have a dipole moment, it must be very small. Only a very dilute solution of phosphorus pentachloride could be made, as the solubility is low. The precision of the molar polarization calculated from the capacity of the solution is, therefore, not very high.

TABLE II

MOLAR POLARIZATION OF ANTIMONY PENTACHLORIDE IN SOLUTION IN CARBON TETRACHLORIDE

Temp., °C	Dielectric constant	Density, g./cc.	Molar polarization in cc Of solution	Of $SbCl_5$
6.5	2.326	1.72191	30.1	47.6
14.0	2.313	1.70780	30.1	47.6
25.1	2.294	1.68592	30.2	48.5
40.4	2.267	1.65578	30.3	49.5
46.9	2.254	1.64260	30.3	49.5

Mole fraction of $SbCl_3$............0.105

TABLE III

MOLAR POLARIZATION OF PHOSPHORUS PENTACHLORIDE IN SOLUTION IN CARBON TETRACHLORIDE

Temp., °C.	Dielectric constant	Density, g./cc.	Molar polarization in cc. Of solution	Of PCl_5
8.9	2.253	1.62638	28.2	33
21.9	2.226	1.60128	28.2	33
31.85	2.206	1.58230	28.2	33

Mole fraction of PCl_5............0.0311

The Dielectric Constant of Antimony Pentachloride.—This was determined over a range of temperature, the values being given in Table IV. The molar polarization was calculated from these measurements by means of the Clausius and Mosotti equation. This equation has been used previously for pure non-polar liquids, and so its use in this case is probably justified. These values agree well with those obtained from the capacity measurements of the carbon tetrachloride solution.

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[4] Ref. 2, p. 1006.

[5] Debye, "Polar Molecules," The Chemical Catalog Co., Mew York, 1929, p. 45.

TABLE IV

DIELECTRIC CONSTANT AND MOLAR POLARIZATION OF ANTIMONY PENTACHLORIDE

Temp., °C.	Dielectric constant	Density, g./cc.	Molar polarization, cc.
0.0 crystal	3.3		
2.6 liquid	3.307	2.387	54.1
17.6	3.220	2.356	53.7
19.8	3.222	2.352	53.8
20.9	3.212	2.349	53.7
30.0	3.173	2.331	53.5
38.4	3.136	2.314	53.5
47.2	3.103	2.296	53.4

The Dielectric Constant and Conductivity of Phosphorus Pentachloride.—The dielectric constant of phosphorus pentachloride was found to be as follows: crystal material at 135°, 4.2, and the liquid under pressure at 165°, 2.7. The conductivity of this compound was also measured with the following results

	Specific conductivity
Liquid at the melting point	6×10^{-9} reciprocal ohms
Crystal at 100°	3×10^{-8} reciprocal ohms
Crystal at 20°	3.3×10^{-7} reciprocal ohms

Discussion

The dielectric constant of the crystalline phosphorus pentachloride being greater than for the liquid is a result that is both interesting and unusual. If we apply the method of Errera,[6] which uses the dielectric constant of the solid to determine P_0, in order to calculate the electric moment, we shall have negative values, for $P - P_0$ will be negative. This makes the use of the method of Errera doubtful, for if it is certain that it cannot be used in this case, then its use in any other case is questionable.

A possible explanation for this result is that the crystal forces distort the molecule and increase the polarization, the molecule being symmetrical and without dipole moment in the liquid state. The conductivity measurements also indicate this, for the liquid has a lower conductivity than the crystalline material. The doubt that this casts upon the method of Errera is that molecules of other compounds may be more or less distorted when crystallized.

The zero or very small dipole moment of these compounds suggests a symmetrical structure. This is definitely in favor of a ten electron shell for the central atom with the five chlorine atoms attached by the five electron pairs. The polar formula, $SbCl_4^+Cl^-$, is definitely ruled out and grave doubts are cast on the structure advanced by Prideaux[7] in which three of the chlorine atoms arc held by electron pairs and two held by single

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[6] Debye, "Polar Molecules," p. 53.

[7] Prideaux, *Chem. & Ind.*, 42, 672 (1923).

electrons. Only one structure on this basis could give zero dipole moment and that one would have the three electron pairs in a plane with the two single electron bonds at right angles to this plane. Doubt is cast on this structure from three directions. The substance is diamagnetic, and it is difficult to see how two unpaired electrons on opposite sides of the central atom could neutralize each other's magnetic fields. The molecules dissociate readily to give the trichloride and chlorine, which may indicate that, if there are two chlorine atoms held differently than the other three, they should be adjacent. Chemical reactions such as the hydrolysis with water to form the oxychloride also indicate the same. The double molecule formula, $SbCl_3 \cdot Cl_2$, is ruled out by the vapor density measurements, which show $SbCl_5$ to exist in the gas phase.

Summary

The molar polarizations of antimony pentachloride and phosphorus pentachloride have been measured in carbon tetrachloride solutions and the dipole moments concluded to be either zero or very small.

The dielectric constants of antimony pentachloride and phosphorus pentachloride have been measured for both liquid and crystalline states.

The specific conductivity of phosphorus pentachloride has been measured.

Antimony pentachloride and phosphorus pentachloride are assumed to have a symmetrical structure with a ten electron shell for the central atom.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, U. S. BUREAU OF MINES]

THE ENTROPY AND FREE ENERGY OF METHANE[1]

BY H. H. STORCH[2]

RECEIVED JANUARY 15, 1931 PUBLISHED APRIL 6, 1931

Introduction

In a recent publication[3] C. G. Maier reported a discrepancy of about five entropy units between the entropy of methane as calculated by way of low temperature specific heat data and the third law of thermodynamics, and that obtained from Randall and Gerard's[4] and Randall and Mohammad's[5] work on equilibria in the reactions

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad (I)$$

$$C + 2H_2 = CH_4 \qquad (II)$$

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject, to copyright.)

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

[3] Maier, "Zinc Smelting from a Chemical and Thermodynamic Viewpoint," U. S. Bureau of Mines Bulletin 324 (1930).

[4] Randall and Gerard, *Ind. Eng. Chem.*, *20*, **1335** (1928).

[5] Randall and Mohammad, *ibid.*, 21, 1048 (1929).

In view of the numerous reactions involving methane in which the U. S. Bureau of Mines Experiment Stations are interested, it was considered desirable to recalculate the entropy of methane using the recent measurements of Clusius[6] on the specific heat of methane in the temperature range 10.33–105.3°K.; and to revise the calculations of Randall and his collaborators, using a recent experimental value of the heat of combustion of methane, the specific heat equations given by Eastman[7] for hydrogen, carbon dioxide and water, and for methane the data given by Eucken and Lüde[8] for the temperature range 297.7–481.2°K. ,

Entropy of Methane from Specific Heat Data.—The entropy data given in Table I were obtained by using the data of Clusius,[6] the approximate Debye equation for the range 10.33–0.00°K., the heat of vaporization of liquid methane as calculated from the vapor pressure measurements of Keyes, Taylor and Smith,[9] and finally the equation $C_p = 5.90 + 9.60 \text{ X } 10^{-3}T$ given by Eastman[7] in the range 111.8–298.1°K.

In employing the approximate Debye equation, $C_v = 12\pi^4 N \text{ kT}^3/50^3$, the value of Θ used was that given by Clusius. In the range 10.33–111.8°K. the specific heat curve was extrapolated to cover the region under the cusp in the vicinity of 20.4°K., the entropy of transition at the latter temperature being calculated from the value for the heat of transition as given by Clusius.

Recalculation of Entropy and Free Energy of Methane from Equilibrium Measurements.—The specific heat equations given in Table II were used in recalculating the entropy and free energy of methane, using Randall and co-workers'[4,5] data. The equations are all of the form $C_p = a + bT + CT^2$.

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[6] Clusius, Z. *physik. Chem.*, [Abt. *B*] 3, 41 (1929).

[7] Eastman, U. S. Bureau of Mines Technical Paper 445 (1929).

[8] Eucken and Liide, *Z. physik. Chem.*, [Abt. *B*] 5, 436 (1929).

[9] Keyes, Taylor and Smith, J. *Math. Phys., Mass. Inst. Tech.*, 1, 191–212 (1922). determined the vapor pressure of methane and the densities of the coexisting phases, whence by. use of the Clapeyron equation they calculate the heat of vaporization to be 123 cal./g. or 1968 cal./mole at the boiling point (given by them as 111.52° K.), and 2104 cal./mole at the triple point (89.98° K.). The latter figure is in excellent agreement with a calculation based on the vapor pressure of solid methane in the range 76.89–87.25°K. as obtained by Karwat, *Z. physik. Chem.*, 112, 486 (1924)] and by Freeth and Verschoyle [*Proc. Roy. Soc.* (London), A130, 453 (1931)] in the range 64.78–90.66°K.; and on the heat of fusion as given by Clusius.[6] The heat of vaporization of solid methane calculated from Karwat's measurements is 2326 cal./mole, and combining this with 224 cal./mole for the heat of fusion (at 90.6°K.) given by Clusius, the value 2102 cal./mole is obtained for the heat of vaporization of liquid methane in the vicinity of the melting point. This figure checks that of Keyes, Taylor and Smith within 0.1%. It appears therefore that the datum 1968 cal./mole calculated by the latter authors for the heat of vaporization at the boiling point is to be preferred to 2075 cal./mole calculated from the data of Stock, Henning and Kuss [*Ber.*, 54, 1119 (1921)]. However, it would be very desirable to obtain an accurate redetermination of the heat of vaporization.

TABLE I

ENTROPY OF METHANE FROM SPECIFIC HEAT DATA

Temp. range, °K.	Transition points, and form of methane	Entropy units	Authors of specific heat data
0-10.33	Solid	0.36	Debye equation
10-111.8	Solid A–Solid B at 20.4°K. AH = 18.1 cal./mole	0.89	Clusius
	Heat of fusion at 90.6°K. = 224.0 cal./mole	2.47	Clusius
	Specific heat 10.33–111.8°K.	14.55	Clusius
111.8	Heat of vaporization = 1968 cal./mole	17.60	Keyes, Taylor and Smith
111.8–298.1	Gas	7.52	Eastman
Total		43.39	

TABLE II

C_p EQUATIONS

Substance	a	$b \times 10^3$	$c \times 10^6$	Reference to authors
Graphite	1.22	4.89	−1.11	Eastman[10]
H_2	6.85	0.28	0.22	Eastman[7]
H_2O	8.22	0.15	1.34	Eastman[7]
CO_2	7.70	5.30	−0.83	Eastman[7]
CH_4	4.38	14.17	0.00	Euken and Lüde[8]

A recent determination[11] of the heat of combustion of methane yielded the value 212,728 cal, at 25°, which is in good agreement with the figure chosen by Lewis and Randall.[12] This value combined with 94,250 cal. for the heat of combustion of graphite at 25°, and 68,270 cal. for the heat of formation of liquid water at 25°, yields 18,062 cal. for the heat of formation of methane. Using this figure and the equilibrium constants determined by Randall and Gerard,[4] the following free energy equation for reaction I was obtained

$$AF = -35578 + 14.28T \ln T - 4.03 \times 10^{-3}T^2 - 0.44 \times 10^{-6}T^3 - 51.0T \quad \text{(III)}$$

This equation yields $\Delta F_{298.1} = -26912$ cal/mole. Combining this datum with the free energies of carbon dioxide and of water,[10] *viz.*, $\Delta F_{298.1,\ CO_2} = -93{,}647$ and $\Delta F_{298.1,\ H_2O_{(g)}} = -54{,}467$, the free energy of methane is found to be $\Delta F_{298.1,\ CH_4} = -11{,}625$. Hence, substituting in the equation AF = AH − TAS, −11,625 for AF and −18,062 for ΔH, the entropy change (AS) at 25° is found to be −21.60 entropy units. Using the figures 1.3 and 31.23 for the entropies of graphite[12] and of hydrogen gas,[13] respectively, the entropy of methane is calculated to be 42.16 units at 25°.

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[10] "The Free Energy of Water, Carbon Monoxide and Carbon Dioxide," U. S. Bureau of Mines Circular 6125, May, 1929.

[11] Frederick D. Rossini, *Bur. Standards J. Research*, 6, 37 (1931).

[12] Lewis and Randall. "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

[13] W. F. Giuque, THIS JOURNAL, 52, 4816 (1930).

There is no scarcity of data on direct measurements of equilibrium in reaction II. These data are thoroughly reviewed by Randall and Mohammad[5] and by Egloff, Schaad and Lowry.[14] Despite the number of experimenters and the relatively large amount of data available, in no case is a sufficiently complete analysis of the equilibrium mixture described which would indicate with certainty the presence or absence of hydrocarbons other than methane, . For this reason, the accuracy of the equilibrium constants reported for reaction (II) is not readily determinable. In fact, it is probable that the entropy and free energy of methane as calculated from direct equilibrium measurements are not as reliable as the figures obtained by way of low temperature specific heat measurements. Recalculating the data given by Randall and Mohammad[5] for reaction (11), using the specific heat data of Table II, and the value of $\Delta H_{298.1,\ \mathrm{CH_4}} = -18{,}062$ cal./mole, the free energy of methane is found to be $\Delta F_{298.1,\ \mathrm{CH_4}} = -12{,}542$ cal./mole; whence, using the values of the entropies of carbon and hydrogen previously cited, the entropy of methane at 298.1°K. is 45.26 units. This value is 1.87 entropy units higher than that obtained from Clusius[6] specific heat data, and 3.10 units higher than that yielded by Randall and Gerard's[4] data on reaction (I).

Using the value 43.39 units for the entropy of methane, the specific heat data of Table II, and —18,062 cal./mole for AH,,,,,, $\mathrm{CH_4}$, the following free energy equation for methane is obtained

$$AF = -15{,}313 - 10.54T \ln T - 4.36 \times 10^{-3}T^2 - 0.11 \times 10^{-6}T^3 - 47.6T \qquad \text{(IV)}$$

Summary

The entropy of methane at 25° as calculated from Clusius' recent low temperature specific heat measurements is 43.39 units. By calculation from equilibrium measurements for the reactions $CO_2 + 4H_2 = CH_4 + 2H_2O$ and $C + 2H_2 = CH_4$, using Eastman's revision of the specific heat equations of carbon, hydrogen, water and carbon dioxide, the measurements of Eucken and Lüde of the specific heat of methane in the range 297.7–481.2°K., and a recently determined (by the U. S. Bureau of Standards) experimental value of the heat of combustion of methane, the figures 42.16 and 45.24 entropy units, respectively, were obtained. The value 43.39 entropy units as calculated from specific heat measurements is close to the average of the two data calculated from equilibrium measurements and is considered to be the most reliable estimate available at present. A free energy equation for methane based on this entropy figure is presented.

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[14] Egloff, Schaad and Lowry, J. *Phys. Chem.*, *34*, *1617 (1930)*.

[CONTRIBUTION FROM THE AMERICAN CYANAMID COMPANY, NEW YORK CITY]

CALCIUM OXALATE FROM CALCIUM CYANAMIDE

BY GEORGE BARSKY AND G. H. BUCHANAN

RECEIVED JANUARY 16, 1931 PUBLISHED APRIL 6, 1931

The hydrolysis of calcium cyanamide to ammonia and calcium carbonate is a well-known industrial chemical reaction. The hydrolysis of alkali and alkaline earth cyanides to ammonia and salts of formic acid is also familiar. The reactions, expressed in their simplest form, are shown in the equations

$$CaCN_2 + 3H_2O = 2NH_3 + CaCO_3 \qquad (1)$$
$$Ca(CN)_2 + 4H_2O = 2NH_3 + Ca(COOH)_2 \qquad (2)$$

The present paper describes a new reaction, namely, that when a mixture of cyanamide and cyanide is subjected to alkaline hydrolysis there is formed in addition to carbonate and formate, a substantial amount of oxalate, the reaction being expressed by the equation

$$2CaCN_2 + Ca(CN)_2 + 10H_2O = 6NH_3 + 2CaC_2O_4 + Ca(OH)_2 \qquad (3)$$

In a previous communication[1] the present authors discussed the reaction in which cyanamide is converted to dicyandiamide. It was there shown that, confirming the conclusions of Grube and Krüger,[2] this polymerization is a reaction between cyanamide ions and cyanamide molecules and that, consequently, the rate of the reaction is a function of the hydrogen-ion concentration. It was shown that theoretical considerations require that this rate be at a maximum at P_H 9.6, and this calculated value for the optimum hydrogen-ion concentration was confirmed by experiment. The dicyandiamide-forming reaction is represented by the equation

$$NHCN^- + NH_2CN = NHCNHNHCN^-$$

Turning to the behavior of the second component of the reaction mixture, namely, hydrocyanic acid, we have another compound whose polymerization is known to be influenced by hydrogen-ion concentration. Although no quantitative data on the subject are available, it is known that solutions of hydrocyanic acid which have been slightly acidified are stable almost indefinitely. Solutions made strongly alkaline, *i. e.*, solutions of sodium cyanide containing no free hydrogen cyanide, are also stable. On the other hand, solutions of hydrocyanic acid made faintly alkaline polymerize rapidly, depositing brown flocks of the so-called azulmic compounds. We have at present under way an investigation of the polymerization of hydrocyanic acid in aqueous solution which is expected to show that this polymerization, like the polymerization of cyanamide, is also essentially a reaction between ion and molecule.

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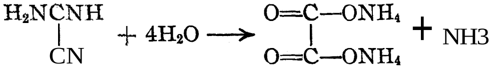
[1] Buchanan and Barsky, THIS JOURNAL., 52,195 (1930).

[2] Grube and Krüger, *Z. physik.* Chem., 85, 65 (1913).

That a reaction of the same type takes place between cyanamide and cyanide is shown in the present paper. This reaction may perhaps be represented by the equation

$$H_2NCN + HCN \longrightarrow H_2NCNH{-}CN$$

This hypothetical intermediate was not isolated; it hydrolyzes readily to form ammonium oxalate according to the equation



$$\begin{matrix} H_2NCNH \\ | \\ CN \end{matrix} + 4H_2O \longrightarrow \begin{matrix} O{=}C{-}ONH_4 \\ | \\ O{=}C{-}ONH_4 \end{matrix} + NH3$$

The existence of the intermediate is shown by the fact that mixtures of cyanamide and cyanide allowed to react at 50° in the absence of lime salts must be boiled with hydrochloric acid before precipitating the oxalate if concordant results are to be obtained. When the boiling is omitted, irregular, low results are obtained.

The reaction described may be considered to be a sort of mixed polymerization. Just as cyanamide, given the proper conditions of hydrogen-ion concentration, reacts with itself to give dicyandiamide, and hydrocyanic acid reacts to give the brown azulmic bodies, so can cyanamide and hydrocyanic acid react with each other, this reaction also being influenced by the hydrogen-ion concentration of the solution in which it takes place.

Experimental Part

During the course of experimental work on the autoclaving of the crude calcium cyanide made by fusion of crude calcium cyanamide and salt, it was observed that, in addition to calcium formate, traces of calcium oxalate were always produced. When pure cyanides were autoclaved, no oxalate was obtained, During the attempt to run down the source of this oxalate it was recalled that the crude calcium cyanide contained small amounts of cyanamide; it was then discovered that the autoclaving of mixtures of calcium cyanide and calcium cyanamide greatly increased the production of oxalate. No oxalate is produced when calcium cyanamide is autoclaved alone.

TABLE 1

RESULTS OF EXPERIMENTS

Mixture, run no.		Weight used in grams	Grams $Ca(COOH)_2 \cdot H_2O$ in cake
1	Crude calcium cyanide	25.0	0.025
2	Calcium cyanamide	31.5	None
3	Crude calcium cyanide	25.0	9.12
	Calcium cyanamide	31.5	
4	Crude calcium cyanide	25.0	3.91
	Dicyandiamide	10.4	
5	Sodium cyanide (97%)	12.6	3.66
	Dicyandiamide	10.4	

In the first experiments the solids were stirred up in 150 g. of water and the mixture was autoclaved for two hours at 75 pounds' steam pressure. The mixture was then filtered and the cakes analyzed for oxalate. In the case of mixture No. 5 where no lime was present, calcium chloride was added to precipitate the oxalate.

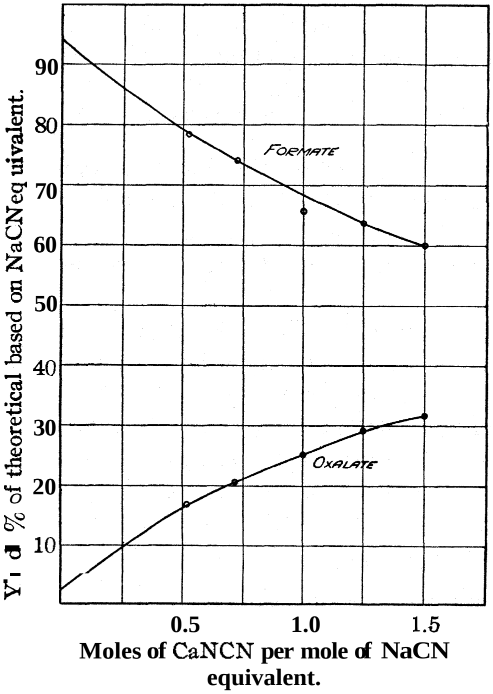


Fig. 1.—Effect of mole ratio on yield.

It is seen that dicyandiamide as well as cyanamide yields oxalate when autoclaved with a cyanide.

Continuing the experiments with crude calcium cyanide and calcium cyanamide, various mixtures of the reactants were autoclaved. The experimental procedure consisted in mixing the solids with water and autoclaving for two hours at 75 pounds' steam pressure. Upon removal from the autoclave the mixtures were filtered and calcium oxalate was determined in the filter cakes.

The results are given in Table II, where the amounts of oxalate found are reported and the yields of oxalate from cyanide are calculated on the assumption of reaction according to Equation 3. The data are also shown graphically in Fig. 1.

The crude calcium cyanide used contained approximately 48.5% $Ca(CN)_2$; the calcium cyanamide, 59.6% $CaCN_2$.

The total yield of oxalate and formate is less than 100% in all cases,

Table II

Experimental Data

Crude $Ca(CN)_2$, g.	Calcium cyanamide, g.	H_2O, cc.	Molar ratio CaNCN/NaCN[a]	$CaC_2O_4 \cdot H_2O$ formed G.	$CaC_2O_4 \cdot H_2O$ formed Yield on NaCN, %	$Ca(COOH)_2$ formed G.	$Ca(COOH)_2$ formed Yield on NaCN, %	Yield, total, %
25.0	15.8	150	0.52	6.08	16.8	12.7	78.5	95.3
25.0	23.6	150	0.72	7.41	20.5	12.0	74.2	94.7
25.0	31.5	150	1.00	9.12	25.0	11.5	65.6	90.6
25.0	39.4	150	1.25	10.55	29.2	10.3	63.7	92.9
25.0	47.3	150	1.48	11.33	31.3	9.7	60.1	91.4

[a] For convenience we use % NaCN equivalent instead of % $Ca(CN)_2$.

partly if not entirely because of loss of hydrocyanic acid by volatilization and by azulmic formation. The oxalate yield cannot be accounted for if we assume it is derived from cyanide alone or from formate alone. The increasing yield of oxalate with increasing amounts of cyanamide added is additional proof that cyanamide takes part in the reaction.

Effect of Hydrogen-Ion Concentration.—The data show that the oxalate yield based on cyanide increases as the amount of calcium cyanamide used is increased. The reasons for this are apparent if the previous work on the polymerization of cyanamide is recalled. The *P*H of a filtered solution of the reaction mixture is 9.8, which is very near the optimum *P*H for dicyandiamide formation. In other words, we are dealing with competing reactions, one involving dicyandiamide formation and the other the formation of the complex which eventually decomposes to form oxalate. The experiments given in Table I show that the oxalate yields from cyanide and dicyandiamide are low,

This suggested that the reaction be conducted at a *P*H less favorable to dicyanadiamide formation and led to an attempt to investigate the effect of hydrogen-ion concentration upon the oxalate forming reaction by following its course in buffered solutions. The technique of these experiments was the same as that employed in our study of the polymerization of cyanamide.[1]

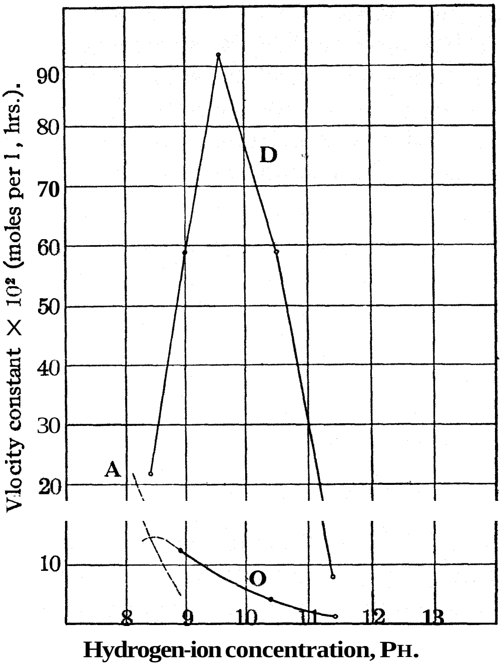


Fig. 2.—Effect of hydrogen-ion concentration. A, azulmic; D, dicyandiamide; O, oxalate; temp., 50° C.

The study proved very difficult, particularly in solutions of lower alkalinity than *P*H 9. The solutions discolored badly due to azulmic formation and there were large losses of hydrocyanic acid by vaporization. The data obtained are therefore only approximate and are presented with this qualification. The results are shown in Fig. 2. The curve for dicyandiamide is taken from our work on cyanamide.[1] The heavy portions of the oxalate curve represent out best experimental data; the broken portions present the less accurate values.

It is apparent from these data that little can be done toward increasing the yield by conducting the experiments at higher or at lower *P*H's than the normal PH of the reaction mixtures. At higher *P*H's cyanide is stable but dicyandiamide formation is rapid. At lower *P*H's cyanide is lost by azulmic formation. At *P*H's at which oxalate formation is most rapid it is accompanied both by dicyandiamide formation and by azulmic decomposition. The reason is, of course, that the ionization constants of hydrocyanic acid and of cyanamide are so nearly alike that it is impossible to have cyanide ions in the presence of cyanamide molecules without having hydrocyanic acid molecules and cyanamide ions present as well.

That reduction of the PH is right in theory was also shown by a few experiments in which calcium chloride was added to the reaction mixture. The purpose was to reduce the PH to a more favorable value by reducing the solubility of calcium hydroxide to which the alkalinity of the solution is due. The results are given in Table III.

TABLE III

25 *g*. of crude calcium cyanide; 31.5 g. of calcium cyanamide; 150 cc. of water; 2 hours at 75 pounds' pressure

Mixture	$CaCl_2$ in mixture, g.	Dry cake, *g*.	Calcium oxalate % in cake	Calcium oxalate o.	Calcium oxalate Yield calcium on NaCN, %
[a]	0	...	...	..	25.0
1	11.7	48.24	21.33	10.3	28.5
2	35.0	55.13	21.78	12.0	33.1

[a] From Table II.

The practical significance of this moderate increase of oxalate yield by the addition of calcium salts is derived from the fact that the solutions obtained by the autoclaving of mixtures of cyanamide and cyanide contain large amounts of formate which is formed from that part of the cyanide which does not react with cyanamide. The return of this solution to a succeeding autoclave charge is practical and was adopted as regular procedure.

Stage Addition of Cyanamide.—The results of some preliminary experiments indicated that small concentrations of cyanamide were more effectively employed in the reaction with cyanide, presumably because less of other products were formed from the cyanamide. That is, the reaction of cyanamide to form dicyandiamide is accelerated by increased concentration to a greater extent than is the formation of oxalate. By keeping the concentration of cyanamide low, that is, by continuous addition of calcium cyanamide, we should expect a higher oxalate yield from a given amount of cyanamide than if the cyanamide were all added at once. This method of adding the cyanamide was followed in experiments described below.

Mixtures were digested for six hours at 60 and 80° in a constant temperature bath. The mixtures were stirred continuously during the digestion. Four samples were run at each temperature.

Twenty-five grams of crude calcium cyanide was added in each case to 150 cc. of water heated to the temperature at which the digestion was to be carried out. They were then placed in the water-bath and the stirrers started. To one pair of the mixtures 31.5 g. of calcium cyanamide was added immediately. To the second pair the 31.5 g. of calcium cyanamide was added in twelve equal portions at half-hour intervals.

At the end of six hours' digestion, one of each pair of mixtures was analyzed directly. The two remaining samples were autoclaved for two hours at 75 pounds' pressure.

During the preliminary digestion some cyanide was lost due to volatilization of hydrogen cyanide formed by hydrolysis.

Table IV

25.0 g of crude calcium cyanide; 31.5 g. of calcium cyanamide; 150.0 cc. of water

Digestion			Subsequent to six hours' digestion	Cake, g.	% in cake	Calcium oxalate	
Time, hours	Temp., °C.	Addition of calrium cyanamide				Grams total	% yield on NaCN
6	60	All at start	Not autoclaved	45.04	13.16	5.92	16.3
6	60	Continuous[a]	Not autoclaved	42.99	14.56	6.25	17.3
6	60	All at start	Autoclaved	46.45	18.42	8.57	23.7
6	60	Continuous	Autoclaved	49.40	20.67	10.22	26.3
6	70	All at start	Not autoclaved	46.50	13.50	6.28	17.4
6	70	Continuous	Not autoclaved	44.86	17.88	8.01	22.2
6	70	All at start	Autoclaved	47.07	19.90	9.36	25.9
6	70	Continuous	Autoclaved	46.80	24.26	11.38	31.4
6	80	All at start	Not autoclaved	44.23	16.20	7.29	20.1
6	80	Continuous	Not autoclaved	46.19	22.30	10.30	29.2
6	80	All at start	Autoclaved	47.53	19.46	9.25	26.3
6	80	Continuous	Autoclaved	48.04	24.12	11.80	32.9

[a] The continuous addition of cyanamide refers to the addition of small portions of calcium cyanamide at half-hour intervals.

Application.—Although the percentage yield of oxalate from cyanide by this process is low, it does not follow that the process is without commercial value. Where cyanamide is being autoclaved for ammonia production the addition to the autoclave of small amounts of cyanide, itself produced from cyanamide in a previous operation, is not impractical. All of the nitrogen of both compounds is liberated as ammonia and recovered, and a part of the carbon of both compounds is converted into valuable by-products. The autoclave solids ordinarily thrown away may be treated by a comparatively simple process and the valuable calcium oxalate separated from the excess of calcium carbonate with which it is associated. Return of the autoclave solution to a subsequent operation provides the excess of soluble calcium salts which has been shown to have a favorable influence on the reaction.

The process above described is protected by U. S. Patent No. 1,717,353, assigned to the American Cyanamid Company. The thanks of the authors

are due to this company for permission to publish these results, and to Mr. K. D. Ashley for his cooperation in the work.

Summary

A reaction not previously reported has been found to take place between cyanamide and cyanide, resulting in the formation of an intermediate compound which can be hydrolyzed to oxalate. The velocity of this reaction is dependent' on hydrogen-ion concentration.

Autoclaving calcium cyanide and calcium cyanamide with water produces calcium carbonate, calcium oxalate and a solution of calcium formate. Replacing the water with calcium formate solution results in increased yields of oxalate.

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ZIRCONIUM. II. ZIRCONIUM OXALATE AND DIPHENYLDINITROGEN ZIRCONIUM

BY HOWARD S. GABLE

RECEIVED JANUARY 19, 1931 PUBLISHED APRIL 6, 1931

Zirconium Oxalate

The fact that an insoluble precipitate was obtained upon the addition of oxalic acid or ammonium oxalate to solutions of zirconyl salts has been known since 1820. Since that time a number of investigations have been made concerning various compounds containing zirconium and the oxalate group, but so far as can be determined there seems to have been no success when efforts were made to obtain the normal zirconium oxalate $Zr(C_2O_4)_2$. The marked success with which the author has prepared other normal zirconium compounds in methyl alcoholic solutions suggested that the oxalate might be prepared in a similar manner.

A methyl alcoholic solution of zirconium tetrachloride was treated with a methyl alcoholic solution of oxalic acid. A reaction took place at once with the formation of a white gelatinous precipitate. This was filtered off, washed, dried and analyzed.

Anal. **Calcd. for $Zr(C_2O_4)_2$: Zr, 34.80. Found: Zr, 35.08.**

The two figures are close enough together to establish the identity of the compound.

The effects of a number of common solvents were observed. They are given below in table form. It is worthy of note that the normal zirconium oxalate is quite soluble in water, quite contrary to what might be expected from the literature, since the basic salts investigated by other workers are noted for their insolubility.

Diphenyldinitrogen Zirconium

The formation of a precipitate upon the addition of aniline to a solution of a zirconium salt has been reported by Alice M. Jefferson.[1] She states that the addition of aniline is accompanied almost immediately by a separation of a beautiful white gelatinous precipitate. The results indicated that the reaction was quantitative. No analytical results as to the composition were given.

Mathews[2] had reported a few years earlier on the formation of an addition compound between aniline and zirconium tetrachloride when aniline was added to an ethereal solution of the zirconium compound. This was a gray precipitate corresponding to the formula $ZrCl_4 \cdot 4C_6H_5NH_2$.

The object of this investigation was to repeat the work by Jefferson, to determine the composition of the precipitate, and to carry out the reaction in methyl alcoholic solution.

An investigation proved that the precipitates obtained in alcoholic and water solutions were identical. The work carried out in methyl alcoholic solution is given below.

An excess of aniline was added to a dilute solution of zirconium tetrachloride in methyl alcohol, and the mixture allowed to stand for several days. On examination a voluminous precipitate was found which was filtered off and washed with methyl alcohol. The filtrate contained an excess of hydrochloric acid, showing that a replacement and not addition reaction had taken place. After drying the precipitate for some time it was analyzed.

Anal. Calcd. for $(C_6H_5N)_2Zr$: Zr, 33.37; N, 10.25. Found: Zr, 33.34; N, 10.40.

These figures indicate that the reaction took place according to

$$2C_6H_5NH_2 + ZrCl_4 \longrightarrow C_6H_5N{=}Zr{=}NC_6H_5 + 4HCl$$

The solubility of the diphenyldinitrogenzirconium was observed in a number of solvents. These are given below with the solubilities of the oxalate.

Solvent	$Zr(C_2O_4)_2$	$(C_6H_5N)_2Zr$
CCl_4	Insoluble	Insoluble
CS_2	Insoluble	Insoluble
C_2H_5OH	Insoluble	Insoluble
CH_3OH	Insoluble	Insoluble
NH_4OH	Insoluble	Insoluble
HCl	Insoluble	Insoluble
$C_6H_5NH_2$	Slightly soluble	Insoluble
HCOH	Reaction	Reaction
H_2O	Very soluble	Insoluble
CH_3COOH	Slightly soluble	Insoluble
$(CH_3)_2CO$	Slightly soluble	Insoluble
HNO_3	Insoluble	Soluble

The reaction was quantitative.

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[1] Jefferson, THIS JOURNAL, 24, 540 (1902).

[2] Mathews, *ibid.*, 20, 815 (1898).

Summary

1. The use of methyl alcoholic solutions allows compounds of zirconium to be prepared without danger of hydrolysis.

2. The normal zirconium oxalate, $Zr(C_2O_4)_2$, was prepared and described.

3. Diphenyldinitrogen zirconium, $(C_6H_5N)_2Zr$, was prepared and described.

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

THE DIELECTRIC CONSTANT OF HYDROGEN CHLORIDE FROM 85 TO 165°K.

BY RICHARD M. CONE, GEORGE H. DENISON AND JACOB D. KEMP

RECEIVED JANUARY 23, 1931 PUBLISHED APRIL 6, 1931

A consideration of the motions of molecules in crystals has led Pauling[1] to conclude that in certain cases there is complete rotation of the molecules at temperatures below the melting point. He also points out that the transition from a condition in which most of the molecules undergo small oscillations about equilibrium orientations, to one in which they rotate completely, may take place over a very small increase of the oscillational quantum number.

Transitions in the solid hydrogen halides involving the absorption of considerable amounts of heat have been reported by Eucken and Karwat[2] and measured accurately by Giauque and Wiebe.[3] The transition in hydrogen chloride[3a] is perfectly isothermal at 98.36°K., and requires 284.3 calories per mole. Pauling associates such transitions with the taking up of rotational energy.

Whenever the molecules of highly polar substances, such as the hydrogen halides, are free to rotate, those substances must have a high dielectric constant. If the transition in hydrogen chloride at 98.36°K. has produced free rotation of the molecules, then the dielectric constant of the solid should increase considerably at that temperature, in accordance with Pauling's prediction. The purpose of this work was to determine whether or not such an increase occurs.

Apparatus and Experimental Procedure

Hydrogen chloride, prepared by allowing C. P. concentrated sulfuric acid to drop on C. P. sodium chloride, was condensed by liquid air. After

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[1] L. Pauling, *Phys. Rev.*, 36, 430 (1930).

[2] Eucken and Karwat, *Z. physik. Chem.*, 112, 467 (1924); Karwat, *ibid.*, 112, 486 (1924).

[3] Giauque and Wiebe, (a) THIS JOURNAL, 50, 101 (1928); (b) *ibid.*, 50, 2193 (1928); (c) *ibid.*, 51, 1441 (1929).

boiling off the product at atmospheric pressure and warming the container to room temperature, there was no evidence of moisture. From this result we concluded that the hydrogen chloride was sufficiently dry for our purpose.

The method of measuring the dielectric constants was similar to that employed by Zahn.[4] A Hartley oscillator, kept at a constant frequency of about 3000 kilocycles, was coupled capacitatively from the plate coil to the grid of a single circuit radio receiver which used two stages of audio frequency amplification. A second Hartley oscillator, tuned by a "Precision" standard condenser of the General Radio Company in parallel with the dielectric cell, was loosely coupled to the first; it was sufficient to have the oscillators a meter distant from one another without electrical connection. UX 201-A tubes were used throughout.

The dielectric cell consisted of two concentric copper cylinders, about 18 mm. in diameter and 90 mm. long, with a capacity in air of 42$\mu\mu$f. The construction is apparent from Fig. 1, which is drawn to scale. At the conclusion of our experiments the cell showed no evidence of corrosion.

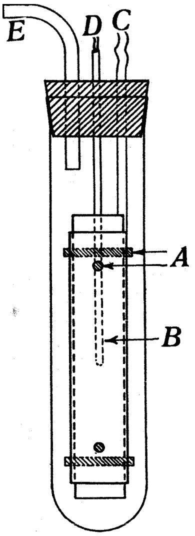

Fig. 1.—A, glass spacers; B, thermocouple tube; C, condenser leads; D, thermocouple leads; E, filling tube.

The solid hydrogen chloride obtained by condensation in liquid air was allowed to melt, and the dielectric cell was immersed in the liquid. The container was closed and the liquid frozen around the condenser. Since freezing began at the outside and at the bottom, and since there was a considerable depth of liquid above the condenser, any cracks formed in the process were probably filled by liquid flowing in from above.

A copper–constantan thermocouple made of wire calibrated in this Laboratory[5] was given us by Professor W. F. Giauque, and was used with a Leeds and Northrup Type K potentiometer for all temperature measurements.

The apparatus shown in Fig. 1 was suspended within a cylindrical lead block of 10 kg. mass, and the whole placed in a Pyrex Dewar flask containing liquid air. A tight cover was fitted to the Dewar flask, and the temperature was lowered to 83°K. by boiling the air at reduced pressure. The liquid air was then sucked out and the apparatus allowed to warm slowly. As a consequence of the large heat capacity of the lead, the temperature rose only about three degrees an-hour at 85°K.; accordingly, except from 95 to 107°K., dry air was blown in to warm the apparatus at the rate of about ten degrees an hour.

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[4] Zahn, *Phys. Rev.*, 24, 400 (1924).

[5] Giauque, Buffington and Schulze, THIS JOURNAL, 49, 2343 (1927).

With one oscillator at constant frequency, the other, without the dielectric condenser, was tuned by the standard condenser until the beat note came to zero frequency. The dielectric cell was then switched in parallel with the standard condenser and the latter retuned until the beat note again became inaudible. The difference between the two settings of the standard gives the capacity of the dielectric cell; the ratio of the capacity of the dielectric cell in hydrogen chloride to its capacity in air is recorded as the dielectric constant of hydrogen chloride. Simultaneous readings were taken of temperature and capacity.

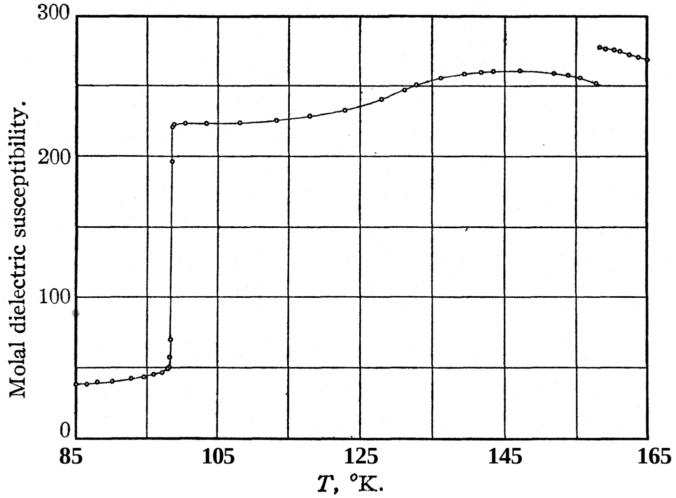

Fig. 2.—Molal dielectric susceptibility of hydrogen chloride.

The accuracy of the temperatures is ±0.1°K., except above 150°K., where an accident to the thermocouple made the accuracy no greater than ±0.4°K. The absolute accuracy of the dielectric constants is probably no better than ±2%, as a consequence of the small capacity of the dielectric cell in air, but variations in the dielectric constant could be followed much more accurately. Of the 135 measurements made, the 40 given in Table I serve to establish the curve of Fig. 2; the deviation of the others from the curve is no greater than that of those shown in the figure.

Results

In Table I are listed for each value of the temperature: D, the dielectric constant; D − 1, which we may call the dielectric susceptibility; $(D-1)M/d$, the molal dielectric susceptibility, where M is the molecular weight and d the density; and P, the polarizability, equal to $(D-1)M/(D+2)d$. In Fig. 2, molal dielectric susceptibility is plotted against T. Values for the density of the liquid are given by the formula d = 1.270 −

0.00276 T, according to Baumé and Perrot.[6] The density of the solid is given by Simon and Simson[7] as 1.469 g./cc. at 107°K. Though the use

TABLE I

DIELECTRIC CONSTANT, DIELECTRIC SUSCEPTIBILITY AND POLARIZABILITY OF HYDROGEN CHLORIDE

T, °K.	Dielectric constant, D	Dielectric susceptibility, D − 1	Molal dielectric susceptibility	Polarizability
84.8	2.595	1.595	39.65	8.629
86.7	2 602	1.602	39.83	8.655
88.0	2.655	1.655	41.13	8.837
90.1	2.676	1.676	41.65	8.910
92.8	2.757	1.757	43.67	9.181
94.6	2.798	1.798	44.68	9.314
96.0	2.869	1.869	46.46	9.542
97.2	2.940	1.940	48.23	9.763
98.0	3.036	2.036	50.60	10.048
98.2	3.083	2.083	51.78	10.187
98.3	3.369	2.369	58 89	10.968
98.4	3.893	2.893	71.91	12.203
98.5	8.893	7.893	196.19	18.011
98.6	9.893	8.893	221 05	18.587
98.8	9.964	8.964	222 83	18.624
100.4	9.988	8.988	223 42	18.637
104.4	9.995	8.995	223.59	18.640
108.2	10.012	9.012	224.01	18.649
113.4	10.083	9.083	225.78	18.686
118.0	10.202	9.202	228.74	18.746
122.9	10.369	9.369	232 88	18.828
128.0	10.679	9.679	240.58	18.975
131.2	10 941	9.941	247.10	19.094
132.9	11.083	10.083	250.64	19.157
136.2	11.274	10.274	255.38	19.239
139.5	11.393	10.393	258.34	19.289
141.8	11.441	10.441	259.52	19.309
143.5	11.464	10.464	260.11	19.319
147.2	11.499	10.499	260.97	19.333
152.0	11.417	10.417	258.93	19.299
154.0	11.345	10.345	257.15	19.269
155.7	11.274	10.274	255.38	19.239
157.9	11.131	10.131	241.82	19.178
158 3	10.845		(HCl is melting)	
158.5	10.643	9.643	277.09	21.917
159.2	10.583	9.583	275.82	21.919
160.4	10.536	9.536	275.31	21.962
161.2	10.488	9.488	274.32	21.966
162.5	10.393	9.393	272.04	21.952
163.8	10.298	9.298	270.37	21.985
165.2	10.202	9.202	268.45	22.000

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[6] Baumé and Perrot, *J. chim. phys.*, 12,225 (1914).

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

of this value for the density at the freezing point is questionable, it is the only reliable one above the transition. A better value may alter the break in the curve at the melting point. This value was also used below the transition, as it is unlikely that the contraction of the solid drew more hydrogen chloride between the plates.

Discussion of Results

The isothermal nature of the change in dielectric constant at 98.4°K. (Table I shows that the change is practically complete over 0.2°K.) was to be expected from the isothermal nature of the transition reported by Giauque and Wiebe[3a] at the same temperature. The suggestion was made by Giauque and Wiebe in reference to hydrogen iodide[3'] that the excitation of only a few molecules may render the low temperature crystal lattice unstable, and that energy is absorbed at the transition to effect a change to a new crystalline form in which another degree of freedom is permitted. If the rotational energy in this new form is sufficiently small, a large fraction of the molecules may take up rotation during the transition. That the higher specific heat above the transition may be due in part to the taking up of this rotational degree of freedom is borne out by the gradual rise in the dielectric constant of the solid between 105 and 150°K. We may conclude from the small change in D on melting that in the solid near the melting point the molecules are rotating almost as freely as in the liquid.

The dielectric constant of the liquid decreases regularly with rising temperature; extrapolation of our curve to 183°K. confirms the value 8.85 found for that temperature by Schaefer and Schlundt.[8] Although our values for the liquid cover too short a range of temperatures to permit the application of Debye's equation, they seem to be in general accord with his theory of dipoles.[9]

We wish to acknowledge our indebtedness to Professor W. F. Giauque for his helpful suggestions in regard to this work.

Summary

The dielectric constant of solid hydrogen chloride has been measured from 85°K. to the melting point, and that of the liquid from the melting point to 165°K. The molal dielectric susceptibility and polarizability have been computed. At 98.4°K., the transition temperature, the dielectric constant changes isothermally from 3 to 10, a behavior which is in accord with Pauling's theory of the rotation of molecules in crystals.

BERKELEY, CALIFORNIA

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[8] Schaefer and Schlundt, *J. Phys. Chem.*, **13**, 669 (1909).

[9] P. Debye, *Physik. Z.*, **13**, 97 (1912).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. IX. THE STANDARDIZATION OF THIOSULFATE SOLUTIONS. DETERMINATION OF THIOSULFATE

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RECEIVED JANUARY 24, 1931 PUBLISHED APRIL 6, 1931

Introduction

It has been demonstrated that ceric sulfate solutions **0.5–3** N in sulfuric acid are stable for long periods of time (at least a year) if prepared from rare earth oxide mixture of suitable grade.[1] Having a standardized ceric sulfate solution available it is desirable to know whether such a solution may be used for checking the normality of a standard thiosulfate solution in the same manner that bichromate or permanganate solution may be used.[2] Ceric ion is reduced readily and completely by iodide ion, and the equivalent quantity of iodine that is liberated may be titrated with thiosulfate in the usual manner. Several investigators[3] have shown that such a process is tedious to carry out experimentally, apparently because the oxidation of hydriodic acid by air is catalyzed by cerous salts. This error may be minimized or eliminated by working with solutions freed from air, in an inert atmosphere (Martin[3]). We have studied this method of standardization of thiosulfate and have found that the presence of a small quantity of ferric ion in the ceric solution causes an additional error which may be minimized by adding a small quantity of phosphoric acid in order to render the ferric ions inactive. In view of all of these complications, we have studied an alternative method which has proved to be excellent.

This alternative method consists in the titration of a measured volume of the thiosulfate solution with ceric sulfate. Direct titration in the absence of iodide is far from stoichiometric, because of the effect of the acid which must be present in the ceric solution, and probably because of the nature of the reaction between ceric and thiosulfate ions as well.[4] If a suitable

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[1] N. H. Furman, THIS JOURNAL, 50,755 (1928); for other papers of this series, see *ibid.*, 50, 1675 (1928); 51, 1128, 1449 (1929); 52, 1443, 2347 (1930). Willard and Young, *ibid.*, 51, 149 (1929); for other papers of the series see, *ibid.*, 50, 1322, 1334, 1368, 1372, 1379 (1928); 51, 139, 149 (1929); 52, 36, 132, 553, 557 (1930); Ind. *Eng. Chem.*, 20,972 (1928).

[2] For references on the use of bichromate, cf. I. M. Kolthoff (translated by N. H. Furman), "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1929, Vol. II, p. 369. For permanganate, cf. W. C. Bray and H. E. Miller, THIS JOURNAL, 46, 2204 (1924); S. Popoff and J. L. Whitman, *ibid.*, 47,2259 (1925). *A* bibliography is given in the latter paper.

[3] Bunsen, *Lieb.* Ann., 105, *40* (1858); Browning, Z. *anorg. allgem. Chem.*, 22, 297 (1899); Martin, THIS JOURNAL, 49,2133 (1927).

[4] Benrath and Ruland found that the direct reaction proceeded approximately according to the equation: $2Na_2S_2O_3 + 2Ce(SO_4)_2 = Ce_2(SO_4)_3 + Na_2SO_4 + Na_2S_4O_6$

amount of iodide is added to the thiosulfate solution, and *if the initial volume is made sufficiently large, disturbing effects are eliminated,* and the titration may be made rapidly and simply to the starch–iodine end-point. The same method of titration may of course be applied to the determination of thiosulfate.

At the start of the titration there is visible liberation of iodine about the entering drops of ceric sulfate, but the iodine is consumed rapidly by the thiosulfate and the blue starch–iodine color does not appear even temporarily if the solution is well stirred until the concentration of thiosulfate is greatly diminished near the end-point.

The reaction $2Ce^{++++} + 2I^- = 2Ce^{+++} + I_2$ proceeds almost instantaneously so that the oxidation of the thiosulfate is effected by the normal reaction: $I_2 + 2S_2O_3^= = 2I^- + S_4O_6^=$. Under these conditions direct interaction of ceric and thiosulfate ions plays a negligible role.

Experimental

The ceric solutions were prepared by dissolving commercial rare earth oxides in sulfuric acid, filtering and diluting to 0.1 N oxidizing power and 1–2 N sulfuric acid concentration.[5] The solutions were standardized against Bureau of Standards sodium oxalate, either potentiometrically or by the iodine monochloride catalytic method of Willard and Young.[5,6]

0.1 N Iodine and thiosulfate solutions were prepared in the usual manner and standardized against Bureau of Standards arsenious oxide, and resublimed iodine, respectively, using starch indicator.[7]

Use of Standard Ceric Sulfate to Determine the Normality of Thiosulfate

Method 1.—The ceric solution was pipetted into a solution containing an excess of potassium iodide; the iodine was titrated with thiosulfate. When air was not excluded, errors of the following magnitudes were found: cc. of approx. 0.1 *N* thiosulfate calcd.. 28.39; cc. found, 28.61–28.81. The end-point was not permanent, nor even moderately stable. If the air is displaced with carbon dioxide, and if no phosphate is present, the error is smaller, but not negligible. For example, we found 28.61, 28.49, 28.51 cc. of thiosulfate; calcd., 28.39 cc. Much better results are obtained if phosphoric acid is added to combine with the iron, the air of course being excluded by carbon dioxide. The solutions were prepared by mixing 60 cc. of potassium iodide solution (20 g. per liter), 25 cc. of sulfuric–phosphoric acid mixture (150 cc. of each of the concentrated acids per liter), and 25 cc. of ceric sulfate, after air had been expelled from the solution: calcd., 23.87 cc.; found, 23.90, 23.92 cc. Under these conditions no ceric phosphate is

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[*Z. anorg. allgem. Chem.*, 114, 267 (1920)]. Our experiments indicate a larger consumption of ceric sulfate per mole of thiosulfate.

[5] Procedure of Willard and Young, THIS JOURNAL, 50, 1322 (1928); 51, 149 (1929). and Furman and Evans, *ibid.*, 51, 1128 (1929).

[6] Furman, *ibid.*, 50, 755 (1928).

[7] The details given by Kolthoff, "Volumetric Analysis," Vol. II, Chap. XII, were followed carefully.

precipitated. Previous experience of one of us (F.) had shown that with pure ceric solutions no phosphoric acid is necessary: calcd., 16.58 cc.; found, 16.60, 16.60 cc.

Our experience is, therefore, in agreement with that of others in finding the method to be accurate if proper precautions are observed. We believe that it is much more tedious and no more accurate than the following one.

Method 2.—Measured volumes of thiosulfate solution are added to a suitable mixture of potassium iodide, starch solution and water and are titrated directly to the starch–iodine end-point with standard ceric sulfate. If the initial volume of the solution is large enough, the acid and the iron which are present in the ceric sulfate solution do not interfere.

There is a lower limit of iodide concentration for any given set of conditions. For example, with an initial volume of 125 cc., containing 25 cc. of approximately 0.1 *N* thiosulfate and 20 cc. of starch (2 g. starch per liter), the following values were found

KI present, g..	0.8	0.4	0.16	0.128	0.08	0.08	0.08
$Ce(SO_4)_2$ soln., cc..	23.42	23.40	23.41	23.43	23.56	23.50	23.55

Correct values (23.41 cc.) were found down to 0.128 g. of potassium iodide. We therefore recommend that at least 0.15 g. of the iodide be present per 125 cc. of initial volume.

Erratic results are obtained if the initial volume of the solution is too small. The summary of results and conditions that is given in Table I will show the magnitude of the errors when the volume is too small.

TABLE I

TITRATION OF THIOSULFATE WITH CERIC SULFATE

	1	2	3	4	5	6	7	8	9
$Na_2S_2O_3$ (0.0956 *N*), cc.	10	10	10	25	25	25	25	25	25
KI, g.	0.4	1.0	1.0	0.1	0.2	0.2	0.3	0.3	0.5
Initial vol., cc.	50	70	100	50	50	100	100	100	100
$Ce(SO_4)_2$ (0.1086 *N*), cc.	8.80	8.83	8.80	22.45	22.30	21.99	21.99	22.03	22.03
$Ce(SO_4)_2$ calcd., cc.	8.81	8.81	8.81	22.01	22.01	22.01	22.01	22.01	22.01
Error, cc.	−0.01	0.02	−0.01	+0.44	\$0.29	−0.02	−0.02	+0.02	+0.02

	10	11	12	13	14	15	16	17
$Na_2S_2O_3$ soln., cc.	50	50	50	50	60	50	50	50
KI, g.	2	1	1	1.6	1.6	1.2	1.6	1.6
Initial vol., cc.	150	200	300	400	400	600	500	500
$Ce(SO_4)_2$ used, cc.	44.48	44.14	44.32	47.37	47.36	47.29	47.26	47.31
$Ce(SO_4)_2$ calcd., cc.	44.03	44.03	44.03	47.28	47.28	47.28	47.28	47.28
Error, cc.	\$0.45	+0.11	+0.29	+0.09	+0.08	+0.01	−0.02	−0.03

NOTE: Determinations 13–17 were made with different ceric and thiosulfate solutions from the others.

A series of determinations with 25 cc. of thiosulfate and initial volumes of 200–300 cc. gave results of 22.01, 22.00, for the 0.0956 *N* solution, and 25.44, 25.46, 25.47 for another solution for which the calculated value was 25.45 cc. If 25 cc. of thiosulfate is used, accurate results are found with initial volumes of 100–300 cc. Note, however, the large errors that result when the volume is 50 cc. (Nos. 4 and 5, Table I). When 50 cc. of thiosulfate is used, the initial volume must be about 500 cc. in order to avoid erratic results (Nos. 15–17, Table I). The error disappears somewhere between an initial volume of 400 and one of 500 cc. If the initial volume is as low as 100 cc. with 50 cc. of thiosulfate taken, errors as large as 0.7 to 1.7 cc. may result. We attribute the erratic values to decomposition of thiosulfate by the acid from the ceric solution, followed by oxidation of the sulfurous acid by either iodine or ceric sulfate. It is possible that the ferric iron (about 1 mg. per 25 cc.) which is present in the ceric solution may cause error when the acidity is high (small initial volume), but we have invariably observed the error to be in the opposite direction to that which would be caused by the iron, and in extreme cases to be three or four times as great as the maximum possible effect of the iron. In general, it appears to be wise to make the initial volume at least 10 times the volume of the thiosulfate used.

The correctness of the method was tested in a preliminary fashion by standardizing both iodine and ceric solutions directly against 25-cc. portions of 0.1000 N arsenious oxide solution prepared from Bureau of Standards arsenious oxide. The normality of the thiosulfate was then determined by titration with the iodine and ceric solutions, respectively.

Standardization of *Ceric* Solution.—Twenty-five cc. portions of arsenite required: 22.67, 22.75, 22.75, 22.68, 22.75, 22.73, 22.77 cc.; average 22.73 cc. equivalent to normality of 0.1100.

Iodine Solution.—Twenty-five cc. of arsenite required: 25.57, 25.58, 25.53, 25.52 cc., average 25.55 cc. Normality 0.0978 (4). Normality of thiosulfate, assuming ceric to be correct: 0.0957, 0.0954, 0.0958, 0.0957, average 0.0957. Normality of thiosulfate assuming iodine to be correct: 0.0958, 0.0959, 0.0960, 0.0959, average 0.0959.

The standardization of ceric sulfate against arsenious oxide was made by Willard and Young's procedure.[8] They found that this procedure gives results about 3 parts per 1000 lower than those found with electrolytic iron or sodium oxalate as a primary standard. Our work was done before the appearance of Swift's paper in which he states that correct results may be obtained in 4 N hydrochloric acid solution with iodine monochloride catalyst: We applied no correction to our results, but if such correction were applied the ceric normality would be 0.1103 and hence the two methods would agree to about 1 part per 1000. Unfortunately, no oxalate standardization of the ceric sulfate solution which we used for this work was made.

A more rigorous check on the fundamental correctness of our-method of standardizing thiosulfate was made with weight buret technique. The Friedman and La Mer type of buret was used and found to be eminently satisfactory.[10]

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[8] Willard and Young, Ref. 5, p. 1372.

[9] Swift and Gregory, THIS JOURNAL, 52, 901 (1930).

[10] Friedman and La Mer, *Ind. Eng. Chem., Anal. Ed.*, 2, 54 (1930).

STANDARDIZATION OF CERIC SULFATE AGAINST BUREAU OF STANDARDS SODIUM OXALATE

	1	2	3	4	5
$Na_2C_2O_4$, g.	0.2047	0.2471	0.2457	0.2116	0.2744
Ceric soln., g.	31.655	38.189	37.977	32.650	42.409
Weight normality	0.09659	0.09657	0.09657	0.096'74	0.09657
				Average,	0 09661 N

Nos. 1, 2, 4 and 5 were made by the iodine monochloride method of Willard and Young;[5] No. *3* was titrated in hot solution containing 20 cc. of concd. hydrochloric acid per 100 cc. Nos. 1–3 were separately weighed samples of oxalate, and Nos. 4 and 5 were weighed aliquot portions of a weighed solution of 1.1270 g. of oxalate.

STANDARDIZATION OF THIOSULFATE AGAINST RESUBLIMED IODINE[11]

	1	2	3	4
Iodine, g.	0.3741	0.6186	0.3379	0.5248
Thiosulfate soln., *g*.	29.787	49.236	26.879	41.736
Weight normality	0.09895	0.09899	0.9905	0.09907
			Average	0.09901 N

TITRATION OF THIOSULFATE WITH CERIC SULFATE

	1	2	3	4	5
Initial vol., cc.	300	300	300	300	500
(1) Thiosulfate soln., g.	20.172	21.924	19.455	18.747	40.252
(2) Ceric soln., g.	20.650	22.452	19.903	19.201	41.184
Ratio [(2)/(1)]	1.0237	1.0241	1.0231	1.0242	1.0231
				Average	1.0236

In Nos. 1–4, 2 g. of potassium iodide, and in No. 5, 4 g. of potassium iodide were present. In each case 20 cc. of 0.2% starch solution was present.

Hence the normality of the thiosulfate found indirectly is 0.09961 X 1,0236 = 0.09889 as contrasted with the directly determined value of 0.09901. The method, therefore, appears to be quantitative to better than 2 parts per 1000 (1.2 parts); the discrepancy between the direct and indirect values is of the same order of magnitude as that of the uncertainty regarding the purity of the sodium oxalate (one part per thousand according to the Bureau of Standards).

Potentiometric Method.—A number of experiments were made potentiometrically; these will not be described in detail. It was found that in the presence of iodide a very small jump in potential, Pt vs. N calomel electrode (about 0.01 volt per 0.05 cc. of 0.1 N ceric sulfate), occurred at the end-point of the reaction. The iodine–starch end-point is much superior in this case.

In the absence of iodide there is no definite potentiometric end-point; no fairly stable high e. m. f. (0.8–0.9 volt, Pt vs. N calomel electrode) is

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[11] The iodine was kept until needed in a stoppered vessel in a desiccator over anhydrous barium perchlorate ("desicchlora"). The lid of the desiccator was not greased.

developed until about a 25% excess of ceric sulfate has been added; the potential is not constant, indicating further reaction. The direct interaction of ceric and thiosulfate ions appears to be rather slow, and the thiosulfate is in part decomposed (by acid) with formation of sulfurous acid (odor of sulfur dioxide).

Determination of **Thiosulfate.**—It is possible to determine thiosulfate in solutions or in salts by titration with standard ceric solution, if potassium iodide is present.

Recommended Procedure.—If approximately 0.1 N ceric solution is used: dissolve 0.5–0.7 g. of crystalline sodium thiosulfate (or an equivalent quantity of any other thiosulfate) in water, add 0.3 to 0.4 g. of potassium iodide, and starch solution (20 cc. of 0.2% solution), dilute to 250 cc. and titrate with ceric sulfate to the starch–iodine end-point.

Eleven students followed a procedure approximately as given in the preceding paragraph, although the importance of the initial volume–concentration relations was not fully realized at the time when this work was done. Working on clear crystals of uneffloresced sodium thiosulfate pentahydrate (Kahlbaum preparation), the following values were found: 63.69, 63.82, 63.90, 63.72, 63.53, 63.82, 63.30, 63.60, 63.61, 63.38, 63.52% $Na_2S_2O_3$ (calcd., 63.71%). In each case the value given is an average of two or more concordant determinations. The majority of the determinations (9 out of 11) are satisfactory.

A number of other possible applications of the use of iodide as a sort of "catalyst with known mechanism" in ceric sulfate oxidations are being studied in this Laboratory. In effect this method makes use of the iodide–iodine system not only as a catalyst but as an oxidation–reduction indicator (with the addition of starch) as well.

Summary

A standard ceric sulfate solution may be used to determine the normality of thiosulfate: (a) by liberating iodine from an iodide and titrating the former with thiosulfate. Air must be excluded, and ferric iron, if present in the ceric solution, must be rendered inactive by means of phosphate, (b) by titration of a mixture of thiosulfate, iodide and starch indicator with ceric sulfate. The initial volume should be ten times that of the thiosulfate used; 0.15 g. of potassium iodide should be present per 125 cc. of initial solution.

The reaction between ceric sulfate and thiosulfate, with intermediate action of iodide, has been shown to be stoichiometric at least to 1.2 part per thousand.

The reaction may be applied to the determination of thiosulfate.

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[CONTRIBUTION NO. 43 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

REACTIONS OF HYDROGEN AND OXYGEN ON PLATINUM WIRES AT LOW TEMPERATURES AND PRESSURES

BY HERBERT G. TANNER AND GUY B. TAYLOR

RECEIVED JANUARY 24, 1931 PUBLISHED APRIL 6, 1931

Introduction

In an attempt to make a study of a well-defined surface for a simple catalytic reaction, pure platinum wire was chosen as the catalyst, and for the reaction, the combination of hydrogen and oxygen to form water vapor. Wire drawn through a series of agate dies is cryptocrystalline. If annealed at dull red heat, strain is removed, but the crystals are still very small. By heating to a temperature near the melting point crystals readily visible to the unaided eye are formed in the wire. A pure platinum wire 0.1 mm. in diameter and 2 meters long was heated by direct current in the air to dazzling white heat for ten minutes. Many single crystals, extending clear across the wire, were about one millimeter long. However, because of the variability in catalytic behavior of every specimen of wire used, it was not possible to establish any relationship between the activity of cryptocrystalline and macrocrystalline wires. Both kinds of wire behaved much alike. In studying these wires some unexpected observations were made and are here presented.

Apparatus

The apparatus was designed to work at a few microns' pressure and is sketched in Fig. 1. It was constructed of 15-mm. Pyrex tubing, except that in some experiments tube C was made of transparent silica attached to the train by a graded seal. The catalyst wire was mounted in tube C and supported by heavy tungsten wires sealed through the glass. These supports were glass-coated except at the tips, where the platinum was spot-welded to the tungsten. The platinum wire, 58 cm. long by 0.10 mm. in diameter (area 1.8 sq. cm.), was used either in the form of a spiral, or of hairpin loops similar in arrangement to the filament in a vacuum Mazda lamp. The distance from the

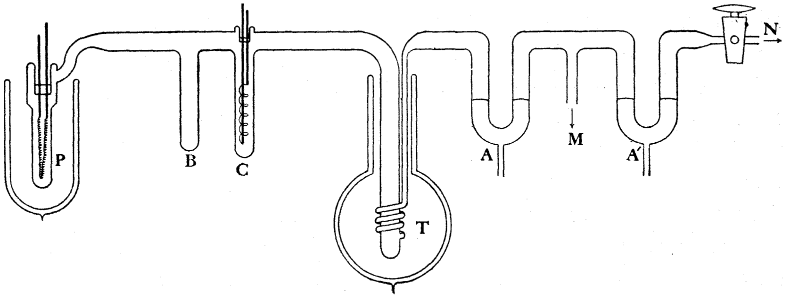

Fig. 1.—Apparatus: M, to McLeod gage; N, to pump and gas reservoirs.

wire to the wall of C was 3 to 4 mm., which is less than the mean free path of the molecules of the common gases at 10 microns' pressure.

The special form of Pirani gage[1] at P was capable of detecting the disappearance of 0.001 cu. mm. of gas, N. T. P., a quantity considerably less than that calculated to form a monomolecular layer of hydrogen on a surface area of one square centimeter. The trap at T was cooled with liquid air or solid carbon dioxide in methanol as occasion required. Mercury cut-offs, **A-A'**, were used instead of stopcocks, and between them was attached a McLeod gage, range 0.01 to 100 microns. The total volume A to P, was about 75 cc.

Prior to a series of experiments and sometimes prior to each experiment, the apparatus was thoroughly baked out by flaming until a vacuum was obtained so low as to be unreadable on the McLeod gage. A small Tesla discharge brushed over the glass parts was found to be very effective in hastening the release of gases from the walls.[2]

The catalyst wire in C was heated electrically by making it one arm of a Wheatstone bridge, and its temperature was calculated from its resistance. The Pirani gage was calibrated against the McLeod gage with pure oxygen, pure hydrogen and electrolytic gas ($2H_2:O_2$). All gases used were carefully purified and stored in glass bulbs sealed to the line beyond the stopcock shown in Fig. 1. The electrolytic gas was generated from potassium–barium hydroxide solution with nickel electrodes. No gas was collected until the generator was evolving a gas mixture in equilibrium with electrodes and solution. The sample collected, 20 cc. N. T. P., furnished all the aliquots used in several hundred experiments.

The usual procedure for determining catalytic activity was to exhaust the apparatus thoroughly, introduce the gas, close A' and read the pressure on both the Pirani and McLeod gages. Then **A** was closed, the wire heated and the pressure change followed with the Pirani gage.

Experimental Results

Nature **of** the Reaction.—In the earlier experiments the platinum wires were never at any time heated above 500°. With electrolytic gas complete clean-up was seldom obtained, pure hydrogen being left when the reaction stopped. Figure 2 shows a typical rate curve with the wire at 90° and the tube wall at room temperature. In common with curves for many other experiments, there is an induction period at the start. This is followed by a section of curve which bends more and more pronouncedly in the opposite direction, not reaching zero pressure as demanded by theory if electrolytic gas reacted quantitatively to form water. The general shape of the curve shows that the catalytic formation of water on platinum is not a simple process.

When an equimolar mixture of hydrogen and oxygen was used, the clean-up was frequently as high as 90% instead of the 75% demanded by theory if water formation were the only reaction concerned. The gas left in this case was pure oxygen. The nature of the residue was easily ascertained by exhausting the McLeod gage, closing **A'**, opening A and then comparing pressures read on the McLeod and Pirani gages. For example, if the actual pressure determined by the McLeod gage fell on the hydrogen calibration

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[1] Tanner. *J. Phys. Chem.*, **34,1113** (1930).

[2] The Tesla coil was found much more effective when locating pinhole leaks if the apparatus contained a low pressure of hydrogen rather than air.

curve of the Pirani gage, introduction of oxygen always caused further reaction. A few typical results are given in Table I.

TABLE I

REACTION OF HYDROGEN–OXYGEN MIXTURES

Gas	Pressures, microns Initial	Pressures, microns Final	Residue
$2H_2 + O_2$	14.4	7.2	H_2
$2H_2 + O_2$	42.3	12.0	H_2
$2H_2 + O_2$	123.0	6.0	H_2
$H_2 + O_2$	19.7	2.2	O_2
$H_2 + O_2$	25.0	2.7	O_2

These results show that considerably more oxygen disappears than corresponds to water formation. This effect has been also noted by Langmuir,[3] who attributed it first to oxidation of gases dissolved in the platinum, but later to evaporation of atoms from the surface and their subsequent combination with oxygen to form ozone, or with water vapor on the bulb walls to form hydrogen peroxide. The hypothesis of reaction with dissolved oxygen does not explain our results because the effect was observed after repeated heating and cooling in pure oxygen. If the atomic oxygen explanation is correct, there should have been a clean-up of oxygen after the reaction with hydrogen ceased, but this was never observed at any temperature used for the catalysis experiments, *i. e.*, up to 380°. Hydrogen peroxide can be formed directly from its elements since its free energy of formation is half that of water,[4] and it seems probable that it is formed directly on the catalyst surface.

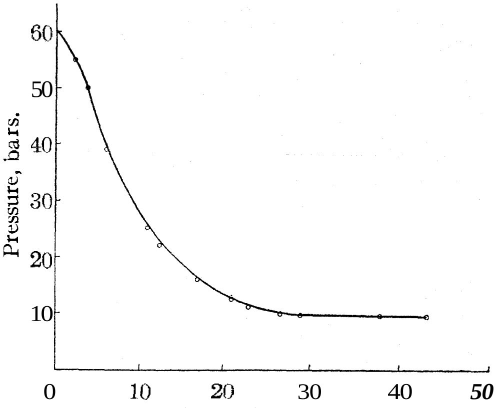

Fig. 2.—Rate of reaction of electrolytic gas on platinum.

The reaction at low pressures of hydrogen and oxygen on platinum has been widely quoted as a conspicuous example of a reaction retarded by one of the reactants.[5] In one series of our experiments, the initial partial pressure of oxygen was kept constant and the hydrogen pressure varied fourfold. The results with the wire at 100° and the wall at liquid-air

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[3] Langmuir, THIS JOURNAL, 40, 1394 (1918); *Trans. Faraday Soc.*, **17**, 621 (1922).

[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 495.

[5] Langmuir, THIS JOURNAL, **37**, 1165 (1915); **38**, 2291 (1916); *Phys. Rev.*, 8, 158 (1916); *Trans. Faraday Soc.*, *17*, 654 (1922).

temperature are shown in Table II. Experiment 1 shows that oxygen in excess of electrolytic gas ratio has an accelerating effect on the reaction.

TABLE II

EFFECT OF VARIATION OF HYDROGEN CONCENTRATION

Initial pressures, bars		Ratio	Final pressure,	Minutes for re-
H_2	O_2	$H_2:O_2$	bars	action to stop
12.5	12.5	1:1	6.5	9
25	12.5	2:1	2.5	45
50	12.5	4:1	24.0	5

Experiment 3 shows that an excess of hydrogen over the amount present in electrolytic gas likewise accelerates the reaction. The composite nature of the reaction is still evident.

At much higher pressures Donnelly and Hinshelwood[6] found the reaction rate to be independent of the hydrogen pressure.

After a wire had been seasoned by use for some time, the abnormal consumption of oxygen tended to disappear. Perhaps a fresh surface is composite, part of it promoting hydrogen peroxide formation and part water formation.

Wall-Temperature Effect.—When the tube containing the catalyst was surrounded by liquid air, the rate of the reaction was surprisingly accelerated. Some acceleration would be anticipated because of the increased concentration[7] of the reactants produced by cooling the tube. From Charles' Law, the increase in concentration by cooling from 298 to 90 Å., would be 3.3 to 1. At pressures where the mean free path is comparable with the diameter of the tube, the increase in concentration is the ratio of the square roots of the temperature—in this case 1.8 to 1. This latter condition was approximately realized in the experiments, so that roughly the increase in concentration was 2 to 1 instead of 3 to 1. The increase in rate due to cooling the catalyst tube, although variable, was frequently as high as sixfold. The rate during the middle part of any one experiment with all temperatures constant changed comparatively little over small pressure differences. The effect is illustrated in Fig. 3. The curve from A to B shows the rate of reaction when the catalyst was at 200° and the wall at room temperature.

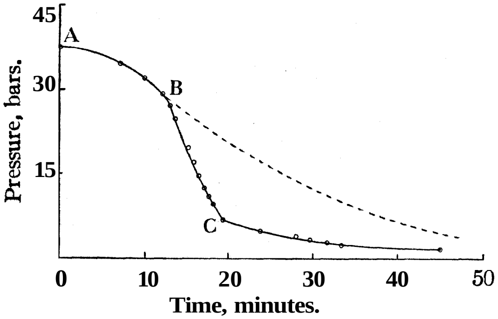

Fig. 3.—Effect of wall temperature on reaction rate of electrolytic gas.

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[6] Donnelly and Hinshelwood, *J. Chem. Soc.*, 1727 (1929).

[7] S. Dushman, *High Vacuum*, 135–36 (1922).

The steep slope of the curve from B to C shows the effect of placing liquid air around the catalyst tube, during which time the catalyst was maintained at 200°. Had no liquid air been used, the rate would have been more nearly described by the dashed line.

Unless the catalyst was specially activated (see below) no reaction occurred upon introducing electrolytic gas into the reaction tube when the catalyst and the tube wall were both at room temperature. If the wire only was heated, usually to 150°, a reaction started, increased in rate quite rapidly for the first few minutes, then settled down to nearly a straight line rate until the end was approached. If, however, the gas was introduced at room temperature and then both the mire and wall were heated simultaneously, no reaction occurred even by the time a temperature of 200° had been reached. If the wire was heated beyond this point and the wall held at 200°, reaction occurred when the wire attained a temperature of 300°.

Again, starting with a fresh sample of gas, with wire and wall at room temperature no reaction occurred. Placing liquid air around the wall did not start the reaction, but when the wire was heated for a few seconds to 100°, the reaction started. Lowering the temperature of the wire to room temperature retarded the reaction but did not stop it until the wall was brought to room temperature by removing the liquid air. When wire and wall were again at room temperature, no reaction occurred. In a qualitative way these effects, with but occasional unexplainable exceptions, could be reproduced.

Other reactions than that between hydrogen and oxygen were investigated, *e. g.*, the hydrogenation of ethylene, the oxidation of carbon monoxide, and the decomposition of nitrous oxide. Changes in the slope of the rate curve upon cooling the catalyst tube were found, but these changes were comparatively small. The wall-temperature effect is masked if the rate of a reaction varies with pressure. Since the rates of the above-mentioned reactions change with pressure, the small accelerations observed when the catalyst tube was cooled are difficult to interpret. All that can be safely concluded is that the wall effect, if shown at all by these reactions, is comparatively small.

The wall-temperature effect shown by electrolytic gas reacting on platinum is independent of the geometrical position of the wire with respect to the wall. In many experiments the catalyst was wound in a short helix and located axially within the tube. In other experiments it was arranged in long hairpin loops.

No difference in the effect was observed with fused silica or Pyrex glass walls.

Gold was substituted for platinum. The higher temperature to which the gold had to be heated to cause electrolytic gas to react, and the added complication of the reaction rate changing rapidly with pressure masked the wall effect. So far as these few experiments apply, the conclusion is reached that any wall effect which gold may show is so small as to be obscured by other complications.

Super-activity.—Along with the study of the wall-temperature effect, experiments were performed in the hope of finding the most potent causes of variability in the activity of the catalyst. The rate curves (for the electrolytic gas reaction) showed high variation from one experiment to the next, and they were not always consistent with each other as to form. Some of the curves were straight lines, others were hyperbolas, and others were S-shaped. The latter were the most frequent. At the start of a reaction the rate would become accelerated, reach a steady state and then decrease. Some of this curvature may be due to the reaction not proceeding to the formation of water only. The induction period portion of the curve may be due to variation in the composite nature of the catalyst surface.

In order to find out whether or not outgassing the wire and apparatus had any important influence on activity, the wire and walls were baked out at about 400° for several hours, during which time the pumps were running. No unusual variation in results was observed. A silica tube was substituted for the glass tube, and the wire catalyst was suspended on silica supports. This was baked out at 700° with pumps running for five hours, but no unusual results were obtained. Next, the catalyst was heated to 900° while the walls were gently heated by a flame for one-half hour during exhaustion. This procedure activated the catalyst so highly that a sample of electrolytic gas reacted while being introduced even though both catalyst and wall were at room temperature. The reaction was nearly complete in two minutes. The rate was so surprisingly rapid in spite of the fact that no temperature difference existed between the wire and wall that measurement of the rate could not be made. It was necessary to cool the wall and catalyst with liquid air before introducing the sample in order to control the reaction. Careful heating of the wire from -180 to $-120°$ initiated a reaction which went from an initial pressure of 10.6 microns to completion in three hours and ten minutes. The pressure was followed to the gage limit of 0.01 micron. As far as we are aware, this is the lowest temperature at which a catalytic reaction has been observed.

Later it was found that this super-active state of the wire could be induced merely by heating the wire for a few seconds (in *vacuo*) to 900°. Another platinum wire catalyst surrounded by a Pyrex wall behaved similarly. This shows that the effect was not peculiar to a particular wire, and that the silica tube was of no consequence.

The super-active state was not permanent. Even when the catalyst tube was kept surrounded by liquid air so that no condensable gas could contaminate the wire, the super-activity had largely disappeared after five hours.

Bone and Wheeler[8] found that platinum was made more active if heated to 165° in pure hydrogen prior to the addition of electrolytic gas. They found that many other catalysts, metallic and otherwise, behaved similarly. Some of these catalysts were given a preliminary heating in oxygen. One sample of porcelain used as catalyst had its activity increased whether heated in hydrogen or oxygen. Another sample was activated only by hydrogen. Oxygen reduced the activity of silver, which fact has been confirmed by Chapman and Hall.[9]

Since platinum could be made super-active by heating *in vacuo* to 900°, in view of the Bone and Wheeler experiments one might expect an even greater degree of activation if platinum was heated to this temperature in hydrogen. The temperature at which reaction began was taken as the criterion for estimating super-activity. No substantial difference was found in this temperature whether the wire was heated *in vacuo,* or in hydrogen at 0.1 mm. pressure, or in oxygen at this pressure. The super-active state could be produced in a cryptocrystalline wire as well as in a macrocrystalline wire. The temperatures at which the reaction of electrolytic gas was initiated varied even in check experiments from −75 to −120°.

In one experiment the wire had to be heated to +60° to start the reaction which would have gone to completion in several minutes had the temperature not been reduced to −35°. During this same experiment if the walls and catalyst were made 0° the reaction stopped. With walls at 0° the catalyst had to be heated to 110° to cause a reaction which stopped if the catalyst was allowed to cool to the same temperature as the wall. If the catalyst was heated to 60°, the reaction would start when the walls were cooled with liquid air. Removal of the liquid air stopped the reaction.

This experiment shows that the wall effect persists when the wire is intermediate between ordinary and superactivity, and indicates that the effect is not dependent primarily upon the degree of activity. At the highest degree of activation the wall-temperature effect has not yet been investigated.

A possible explanation of the temporarily increased activity of the wire by high temperature treatment is the evaporation of surface contaminations caused by diffusion of gases from the interior of the wire. It is well known that nearly all metals contain dissolved gases, principally carbon monoxide and hydrogen, which are difficultly eliminated by any treatment short of melting the metal *in vacuo.* Experiments with platinum completely outgassed by melting are projected.

In any case, the effect of high temperature treatment observed here is

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[8] Bone and Wheeler, *Phil. Trans. Roy. Soc.*, **206A,** 1 (1906).

[9] Chapman and Hall, *Proc. Roy. Soc.* (London), **124A,** 478 (1929).

quite the opposite of that which would be expected from current theories of sintering active metal areas by heat treatment. In the case of finely divided catalysts sintering must effect a reduction of surface and hence lessened activity. In the case of wires,. the macrocrystalline one, whose sintered surface was obvious, was quite equal in activity to a cryptocrystalline one. This fact taken in conjunction with the remarkable activity at −120° of the heat-treated wire shows that sintering is of no consequence, at least in the case of platinum wires.

Summary

1. A study of the hydrogen-oxygen reaction at low pressures on platinum wires has been made.

2. The reaction is not as simple as is commonly supposed. An excess of oxygen may react. This fact is here attributed to hydrogen peroxide formation from the elements.

3. The activity of platinum is variable even under carefully controlled conditions.

4. The rate of this reaction varies with the temperature difference between the wire and the wall of the containing vessel.

5. Flashing the wire at 900° in vacuum, hydrogen or oxygen induces super-activation which decays after some hours. A wire in the superactive condition causes an easily measurable rate of reaction at as low a temperature as −120°.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. III. DOUBLE AND TRIPLE BONDS AND POLARITY IN AROMATIC HYDROCARBONS

BY C. P. SMYTH AND R. W. DORNTE

RECEIVED JANUARY 26, 1931 PUBLISHED APRIL 6, 1931

The electric moments of simple molecules containing double and triple bonds have been investigated with the object of determining the polarities of these bonds and their relations to structure[1] and these results, together with those of Errera for acetylene dihalides,[2] have been examined in the light of electronic theories of valence.[3] The need of further accurate measurements upon molecules in which ethylene and acetylene hydrogens are replaced by hydrocarbon groups has been evident for some time. An unusual opportunity for such measurements arose through the kindness of Professor Donald H. Andrews of the Johns Hopkins University, who

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[1] Smyth and Zahn, THIS JOURNAL, 47, 2501 (1925).

[2] Errera, *Physik. Z.*, 27, 764 (1926).

[3] Smyth, THIS JOURNAL, 51, 2380 (1929); *Chem. Rev.*, 6, 549 (1929).

loaned us pure samples of the phenyl substituted ethylenes and acetylenes prepared in his laboratory by Dr. R. H. Smith. 1,1,1-Triphenylethane also from the Johns Hopkins laboratories has been measured in order to compare the effect of phenyl substitution in a saturated hydrocarbon **with** the effects in the unsaturated.

Method of Determination

The dielectric constants, ϵ, and densities, d, were measured with the apparatus used in previous work,' the former being determined at a wave length of 600 meters. All the determinations were made in solution in benzene, which appeared to be the best non-polar solvent for these substances, with the exception of those upon phenylacetylene, which was more soluble in heptane. The polarizations, P_2, of the polar components of the solutions were calculated by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{c_1M_1 + c_2M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2 and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. The values of P_2 have been plotted against those of c_2 and extrapolated to $c_2 = 0$ to obtain the values of P designated as P,. The values of P_∞ when plotted against $1/T$ should give a straight line, as required by the Debye equation, $P = a + b/T$, in which $a = P_E + P_A$, the sum of the electronic polarization, P_E, and the atomic, P_A, and $b = 4aNp^2/9k$, N being the Avogadro number, 6.061×10^{23}, μ, the electric moment, and k, the molecular gas constant, 1.372×10^{-16}. Unfortunately, the short temperature range within which benzene is liquid renders the location of the $P_\infty - 1/T$ curves inaccurate for these solutions. It has seemed best, therefore, to disregard P_A for these substances and use for P_E the molar refraction for the sodium D line, MR_D, which is slightly higher than P_E, a fact which partially compensates for the neglect of P_A. The pronounced variation of the polarizations of the substituted acetylenes with temperature made it possible to locate the $P_\infty - 1/T$ curves with seeming accuracy but with surprising values for a and b. However, instead of using the constant $(P_\infty - a)T = b$, it is safer to use the quantity (P, $- MR_D)T$ at each temperature and calculate the moment from the relation, $\mu = 0.0127 \times 10^{-18}\sqrt{(P_\infty - MR_D)T}$, which follows from the preceding equation. The values of MR_D were determined experimentally—in the case of the solids, from measurements upon the solutions—and are listed in Table III in the "Obs." column. In the "Calcd." column are given the refractions calculated as the sum of the atomic refractions and those for the

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[4] Smyth, Morgan and Boyce, THIS **JOURNAL**, 50,1536 (1928); Smyth and Morgan, *ibid., 50,1547 (1928);* Dornte and Smyth, *ibid., 52,3546* (1930).

unsaturated bonds. The differences between the observed and the calculated values are given in the column under E. The refractive indices and densities of the two substances which could be measured pure in the liquid state are given in Table I. The values used for the polarizations, P_1, of benzene and heptane were those determined in previous measurement~.~

When $P_\infty - MR_D$ is small, a small variation in P, causes a large variation in μ. It has been pointed out[6] that, in such cases, neglect of P_A may lead to apparent values of μ as large as 0.4 or 0.5 X 10^{-18} when they are really zero. However, the values of P_A found for saturated hydrocarbons[5,7] are so small that their neglect is approximately compensated for by the failure to extrapolate MR to infinite wave length. The values found for ethylene, acetylene and benzene,[6] though small, are sufficient to suggest the possibility that considerable error may arise from the neglect of P_A in the substituted ethylenes and acetylenes, but the closeness of MR_D to P in the cases of phenylethylene and 1,1-diphenylethylene seems to indicate that the effect of P_A is slight. The values for the acetylenes lead to the impossible result, large negative values for P_A, which will be discussed later. The most serious error is that of P_∞, which is magnified by the necessity of working in dilute solution. It is greatest for the difficultly soluble tetraphenylethylene, which, in the one solution deemed worth measuring, gave an apparent value of P_2 lower than MR_D, the probable error being about equal to the difference. The accuracy of the moments is not sufficient to distinguish between a value of zero and one of 0.2×10^{-18}, but it is significant that two of the three substances for which an approximately zero moment is found have molecules which should be symmetrical, while the third, phenylethylene, has not a very unsymmetrical molecule. It seems probable that this latter substance may have a small moment.

Experimental Results

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AND POLARIZATIONS OF POLAR COMPONENTS

	1,1,1-Triphenylethane				Phenylethylene (n_D^{20} 1.54343; d_4^{20} 0.9046)			
Mole fr. of 2 =	0.0196	0.0317	0.0409	0.0726	0.0380	0.0524	0.0677	0.0836
t, °C.		ϵ					ϵ	
10	2.324	2.337	2.342	2.371	2.305	2.308	2.311	2.311
30	2.283	2.296	2.301	2.330	2.266	2.270	2.273	2.275
50	2.241	2.254	2.260	2.290	2.226	2.226	2.232	2.232
70	2.199	2.208	2.216	2.246	2.180	2.180	2.187	2.184

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[5] Smyth and Dornte, THIS JOURNAL, 53, 545 (1931).

[6] Smyth, ibid., 51, 2051 (1929).

[7] Smyth and Stoops, ibid., 50, 1883 (1928).

Table I (*Continued*)

Mole fr. of 2 = t, °C.	0.0196	0.0317	0.0409	0.0726
		d		
10	0.8998	0.9060	0.9106	0.9253
30	.8787	.8853	.8900	.9053
50	.8575	.8643	.8693	.8850
70	.8358	.8430	.8485	.8644
		P_2		
10	87.4	87.5	88.0	86.0
30	87.4	87.2	87.7	85.8
50	86.4	86.7	87.3	85.7
70	85.4	83.5	85.4	84.7

(n_D^{20} 1.54333; d_4^{20} 0.9046)

t, °C.	0.0380;	0.0524	0.0677	0.0836
		d		
10	0.8901	0.8904	0.8908	0.8913
30	.8691	.8695	.8699	.8705
50	.8480	.8483	.8486	.8492
70	.8268	.8268	.8269	.8281
		P_2		
10	35.8	36.3	36.5	36.2
30	36.4	36.9	37.0	36.9
50	36.4	36.0	37.0	36.6
70	33.6	34.2	37.0	35.0

1,1-Diphenylethylene

Mole fr. of 2 = t, °C.	0.0303	0.0387	0.0479	0.0575
		ϵ		
10	2.329	2.335	2.342	2.352
30	2.287	2.292	2.300	2.310
50	2.242	2.246	2.257	2.267
70	2.197	2.202	2.208	2.217
		d		
10	0.8976	0.9001	0.9023	0.9049
30	.8767	.8790	.8816	.8843
50	.8551	.8577	.8605	.8633
70	.8335	.8362	.8391	.8421
		P_2		
10	65.6	65.1	65.0	64.9
30	64.9	64.6	64.6	64.7
50	63.3	62.6	64.1	64.3
70	61.0	61.1	61.2	61.7

Trans-1,2-diphenylethylene

t, °C.	0.0196	0.0325	0.0376	0.0451
		ϵ		
10	2.324	2.335	2.341	2.343
30	2.281	2.293	2.299	2.303
50	2.238	2.250	2.256	2.260
70	2.195	2.204	2.212	2.213
		d		
10	0.8952	0.8989	0.9007	0.9014
30	.8737	.8779	.8795	.8817
50	.8523	.8565	.8583	.8604
70	.8308	.8351	.8369	.8395
		P_2		
10	67.9	67.0	67.0	66.5
30	66.9	66.6	66.8	65.6
50	66.0	65.8	66.3	65.2
70	63.9	63.3	65.1	62.7

Triphenylethylene

Mole fr. of 2 = t, °C.	0.0238	0.0350	0.0493	0.0645
		ϵ		
10	2.341	2.352	2.367	2.381
30	2.299	2.310	2.324	2.341
50	2.255	2.266	2.280	2.299
70	2.210	2.225	2.234	2.257
		d		
10	0.9020	0.9074	0.9142	0.9210
30	.8808	.8866	.8938	.9006
50	.8595	.8656	.8731	.8802
70	.8375	.8442	.8522	.8597
		P_2		
10	94.8	92.1	90.6	89.8
30	94.1	91.7	90.1	90.0
50	92.6	90.8	89.2	89.6
70	91.0	90.5	87.2	89.2

Tetraphenylethylene

t, °C.	0.0135
	ϵ
10	2.322
30	2.282
50	2.239
70	(2.192)
	d
10	0.8998
30	.8788
50	.8576
70	.8358
	P_2
10	110
30	111
50	108
70	(101)

Table I (Concluded)

Phenylacetylene (in Heptane) (n_D^{20} 1 5492; d_4^{20} 0 9300) — Diphenylacetylene

Mole fr. of 2 = t, °C.	0.0269	0.0347	0.0641	0.0887	0.0132	0.0198	0.0285	0.0538
			•			ε		
10	1.957	1.962	1.983	2.002	2.333	2.337	2.347	2.368
30	1.928	1.933	1.954	1.969	2.291	2.299	2.306	2.327
50	1.897	1.900	1.922	1.933	2.245	2.258	2.260	2.284
70	1.864	1.866	1.885	1.897	2.201	2.212	2.216	2.240
			d			d		
10	0.6971	0.6988	0.7043	0.7088	0.8931	0.8953	0.8979	0.9049
30	.6801	.6818	.6870	.6917	.8718	.8741	.8766	.8842
50	.6626	.6644	.6695	.6741	.8503	.8525	.8552	.8631
70	.6447	.6466	.6515	.6560	.8284	.8307	.8337	.8416
			P_2			P_2		
10	48.5	46.8	45.9	46.2	85.0	77.1	73.9	69.4
30	47.8	46.5	46.2	45.1	84.9	79.1	74.6	70.5
50	46.0	43.4	45.4	43.5	80.4	80.2	72.6	69.5
70	42.1	39.3	42.4	41.8	77.5	77.2	71.2	68.9

Table II

Values of (P, − MR_D)T, (P, − a)T, and the Moment

	$(C_6H_5)_3CCH_3$			$C_6H_5CH{=}CH_2$			$(C_6H_5)_2C{=}CH_2$		
T, °A.	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	P,	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
283	88.9	1	0.48	36	0	0	68.8	2060	0.58
303	88.4	1390	.47	36	0	0	67.1	1700	.52
323	87.4	1160	.43	36	0	0	65.4	1260	.45
343	86.2	840	.38	36	0	0	63.7	760	.35

	$C_6H_5CH{=}CHC_6H_5$			$(C_6H_5)_2C{=}CHC_6H_5$		
T, °A.	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	P,	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
283	69.0	1020	0.41	99.0	2490	0.63
303	67.5	330	0.23	97.4	2180	.59
323	66.4	0	0	95.8	1810	.54
343	65.0	0	0	94.8	1580	.51

	$C_6H_5C{\equiv}CH$				$C_6H_5C{\equiv}CC_6H_5$			
T, °A.	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$(P_\infty - a)T$	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$(P_\infty - a)T$
283	51.4	4670	0.87	8600	95.1	8780	1.19	18450
303	49.6	4450	.85	8670	91.8	8400	1.16	18750
323	47.8	4170	.82	8660	87.0	7400	1.09	18450
343	45.6	3670	.77	8440	83.2	6580	1.03	18300

$a = 21.0$, $b = 8610$, $\mu = 1.18 \times 10^{-18}$ $a = 29.9$, $b = 18430$, $\mu = 1.72 \times 10^{-18}$

Table III

Refractions and Electric Moments

	MR_D Obs.	MR_D Calcd.	E	$\mu \times 10^{18}$		MR_D Obs.	MR_D Calcd.	E	$\mu \times 10^{18}$
$(C_6H_5)_3CCH_3$	83.8	83.8	0	0.4	$(C_6H_5)_2C{=}CHC_6H_5$	90.2	83.3	6.9	0.6
$C_6H_5CH{=}CH_2$	36.3	35.1	1.2	0	$(C_6H_5)_2C{=}C(C_6H_5)_2$	115.1	107.4	7.7	0
$(C_6H_5)_2C{=}CH_2$	61.5	59.2	2.3	0.5	$C_6H_5C{\equiv}CH$	34.92	33.5	1.4	0.83
$C_6H_5CH{=}CHC_6H_5$	66.4	59.2	7.2	0	$C_6H_5C{\equiv}CC_6H_5$	64.1	57.6	6.5	1.12

Discussion of Results

It is interesting to compare the small moment 0.4 X 10^{-18} found for 1,1,1-triphenylethane with those of other phenyl substituted ethanes and also methanes. The moments of methane[S] and ethane[1] have been found to be zero. When one methane hydrogen is replaced by phenyl to form toluene,[9] a moment of 0.4 X 10^{-18} results. This moment is presumably the resultant, in part, at least, of small displacements of charges in the benzene ring. Because of the symmetry of the ring,[10] it probably acts in the direction of the line joining the ring to the methyl carbon, which lies in the plane of the ring. When a second methane hydrogen is replaced by a phenyl group to form diphenylmethane, a second doublet is introduced which, if the tetrahedral valence angles of the methane carbon are maintained, should give a slightly larger moment to the molecule. Estermann's[11] value 0.37 X 10^{-18} for diphenylmethane is not sufficiently accurate to show whether the moment is really larger or smaller than that of phenylmethane or toluene. This is shown by the fact that his measurements on diphenyl, which should have zero moment,[12] merely indicate the moment to be less than 0.4 × 10^{-18}. The application of the same arguments concerning structure to triphenylmethane leads to the conclusion that it should have the same moment as toluene, 0.4 X 10^{-18}, which has been found to be the case.[13] Actually, the well-known abnormal behavior of the triphenylmethyl radical would lead one to expect a displacement of the charges between the methane carbon and its one remaining hydrogen with resulting alteration of the moment. However, no such alteration is evidenced in the value for triphenylmethane, which is consistent with the absence of any regular differences in the moments of triphenylmethyl chloride and alcohol as compared to-those of the normal and the tertiary butyl compounds.[5] As it has been shown[3,14] that a hydrogen attached to an aliphatic carbon in a hydrocarbon may be replaced by a methyl group without alteration of moment, the moment of 1,1,1-triphenylethane should be the same as that of triphenylmethane as actually observed.

Although all of these values for the substituted methanes and ethanes are inaccurate from the same causes as those to which the probably smaller uncertainties of the results in Table III are due, they show that electrical dissymmetry arises when an aliphatic hydrocarbon group is attached to a

[8] Sanger, *Physik. Z.*, 27, 556 (1926); Riegger, *Ann. Physik*, 59, 753 (1918).

[9] Williams, *Physik. Z.*, 29, 174 (1928).

[10] Smyth and Morgan, THIS JOURNAL, 49, 1030 (1927).

[11] Estermann, *Z. physik.* Chem., *[B]* 1, 134 (1928).

[12] Ref. 9, p. 271.

[13] Sack, *Ergebnisse Exakten Naturwissenschaften*, 8, 307 (1929); Lautsch, Z. *physik. Chem.*, [B] 1, 115 (1928).

[14] Smyth, THIS JOURNAL, 46, 2151 (1924).

benzene ring, but give no evidence of a resultant displacement of charges in the bonds of these groups. This latter is in marked contrast to the considerable differences in chemical behavior observed.

Smyth and Zahn[1] have found zero moment for the ethylene molecule, but a moment of 0.37×10^{-18} for ethylethylene. This is in contrast to the absence of moment when the carbon chain of a paraffin is lengthened,[4] and is indistinguishable experimentally from the moment produced when a methyl or ethyl group is substituted for a hydrogen on a benzene ring. One would look for a moment in phenylethylene, but the experimental results indicate a zero value, although, as previously pointed out, their accuracy is not such as to preclude the possibility of a moment somewhat smaller than 0.4×10^{-18}. The dissymmetry in 1,1-diphenylethylene is sufficient to give rise to a moment of 0.5×10^{-18}, while, in the *trans*-1,2-diphenylethylene, the moment is zero as in the trans-acetylene dihalides investigated by Errera.[2] It is curious that the value found for triphenylethylene should be higher than that for the more unsymmetrical 1,1-diphenylethylene, but the difference is probably not significant. The value for the symmetrical tetraphenylethylene is apparently zero, as would be expected from its symmetry.

It was hoped at the beginning of this investigation that the substitution of a phenyl group for a hydrogen on a doubly-bonded carbon might have a marked effect upon the moment. However, although the exaltation of refraction usually found in conjugated systems given in the column under E in Table III shows a loosening of the electron binding,[15] no abnormal dissymmetry in the arrangement of the charges is apparent. In fact, there is no evidence of a measurable polarity inherent in the double bond itself apd the attachment of hydrocarbon groups to it appears to have about the same effect upon the moment as a similar attachment to a benzene ring. The Kekulé formula for benzene has been indicated to be correct in so far as it places the carbons at the corners of a regular hexagon and the immediately attached atoms in the same plane.[10,16] In view of the mobile double bonds which this formula contains and of the fact that the benzene ring may take part in the formation of-a conjugated system, it is suggestive that the substitution of a hydrocarbon group for a hydrogen on a doubly-bonded carbon gives rise to a moment of the same magnitude as that resulting from a similar substitution on a benzene carbon.

Judging from these results and the fact that acetylene has been found to have zero moment,' one would expect a small moment for phenylacetylene and a zero value for the seemingly symmetrical diphenylacetylene,

[15] Smyth, *Phil. Mag.,* 50,361 (1925).

[16] Williams, *Chem.* ***Rev., 6,*** *589* (1929); Lonsdale, *Proc. Roy. Soc.* (London), **123A,** 494 (1929); Hendricks, *Chem. Rev.,* 7,431 (1929).

instead of which Table III shows a considerable moment for phenylacetylene and a larger one for diphenylacetylene. In Table II, the values of $(P_\infty - MR_D)T$ and the values of the moment calculated from them, instead of being constant as they should be, have a tendency to fall off with rising temperature. With all the substances except the substituted acetylenes, the change in polarization is so small that the change in (P, $-MR_D)T$ and μ, although relatively large, cannot be regarded as definitely significant. However, the polarizations of the acetylenes vary more with temperature. If P, is plotted against $1/T$, a straight line results from which are obtained the values of a, b and μ shown at the bottom of the data for each of the two substances in Table II. The constancy of the values for (P, $- a)T$ = b testifies to the linearity of the curves and the seeming consistency of the results. It must be remembered, however, that a = $P_E + P_A$. The values found for a are much lower than those in Table III for MR_D, which is approximately equal to P_E, and, accordingly, lead to large negative values for P_A, which are impossible. It seems best, therefore, to disregard the value of μ calculated from b and use the mean of the values calculated from (P, $-MR_D)T$ as an approximate indication of the moment.

Evidence of a tautomerism for acetylene and its derivatives, $HC{\equiv}CH \rightleftarrows H_2C{=}C$, was obtained by Nef[17] and later investigators,[18] but Biltz has criticized this evidence and argued against the supposition of the acetylidene form.[19] It is evident that the second structure containing bivalent carbon is unsymmetrical and should possess a considerable moment. The zero moment found for acetylene does not preclude the possibility of the existence of a small fraction of the molecules in the unsymmetrical form, the number of these molecules being too small to have a detectable effect upon the dielectric constant. It would appear that the replacement of a hydrogen by a phenyl group increases the tendency to give the unsymmetrical form, which is still further increased in diphenylacetylene, the behavior being analogous to that of the halogen-substituted acetylenes. The observed moment would thus be the effective mean of those of the two forms. As change in temperature would shift the tautomeric equilibrium, the apparent falling off of moment with rising temperature could be explained by increase in the proportion of the symmetrical form. The uncertainty connected with the temperature variation of the moments weakens it as evidence of the tautomeric equilibrium, but the considerable size of the moments found definitely requires the existence of an unsymmetrical molecule in mono- and diphenylacetylene.

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[17] Nef, Ann., 298, 332 (1897).

[18] Lawrie, Am. *Chem.* J., 36, 487 (1906); Ingold, *J. Chem. Soc.*, 125, 1528 (1924).

[19] Biltz, Ber., 46, 143 (1913).

Summary

The dielectric constants and densities of dilute solutions of the phenyl substituted ethylenes and acetylenes have been measured between 10 and 70°, the molar refractions of the substances have been determined and the data used to calculate the electric moments of the molecules.

The phenyl substituted ethylenes have small or zero moments according to the symmetry of their arrangement about the double bond, showing that there is no measurable polarity inherent in the bond itself. The replacement of a hydrogen on a doubly-bonded carbon by a hydrocarbon group gives rise to a moment of the same magnitude as that which results from a similar replacement in benzene.

The considerable moment found for phenylacetylene and the still larger value for diphenylacetylene, acetylene itself having no moment, give evidence of unsymmetrical molecules and may be explained in terms of a tautomeric equilibrium between a symmetrical form and an unsymmetrical containing bivalent carbon as proposed by Nef, the shift of equilibrium with temperature perhaps causing the temperature variation of the moment observed.

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

THE EFFECT OF AN ELECTRIC FIELD ON FLAMES AND THEIR PROPAGATION[1]

BY BERNARD LEWIS[2]

RECEIVED JANUARY 27, 1931 PUBLISHED APRIL 6, 1931

The knowledge that flames conduct electricity goes back many years. As early as 1801, Volta showed that the leaves of a gold-leaf electroscope diverge when burning charcoal is brought in contact with the knob. Many researches followed for the purpose of measuring the electrical conductivity of flames. It was found that the gases which emerge from the flame are conductive for some time afterward and furthermore, that this property of conduction can be lessened or removed by passing the gases through an electric field of appropriate strength. Complete accounts of these early researches are to be found in Wiedermann's "Elektricität,"[3] in a paper by de Hemptinne,[4] and in the "Handbuch der Experimentalphysik."[5]

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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

[3] Wiedermann, "Elektricitiit," Vol. 4B, Chapter 4, 1898.

[4] De Hemptinne, *Z. physik. Chem.*, 12, 244–274 (1893).

[5] "Die Elektrischen Eigenschaften der Flamme," by H. Becker, Vol. 13, 1929.

For some time attention was directed to the question whether ionization in the flame is of a chemical or thermal origin.[6] The earlier investigations recognized that ionization could not result from chemical action alone, while Garner[6] ascribes the ionization mainly to thermal origin on the basis of calculations using the Saha equation,[7] which postulates a thermal equilibrium between atoms, ions and electrons. Haber,[8] on the other hand, believes that the heat energy of an explosive reaction is not sufficient to account for the observed ionization currents. He suggests that ionization is brought about by collisions of the second kind between energy-rich products of the reaction and molecules possessing low ionization potentials. Although Haber's suggestion finds support in the spectroscopic detection of such groups as OH, CC and CH in flames, the origin of ionization in flames still remains open to further experimental investigation.

A number of attempts were made[9] without success to arrest the propagation of a flame by means of an electric field. About the same time, Malinowski[10] announced that he had arrested a 2.8% benzine (C_6H_{14})–air mixture in a transverse electric field. Later, Bernackyj and Retaniw[11] and Malinowski and Lawrow[12] found that not only the flame of a benzine–air mixture but also that of an acetylene–air mixture could be extinguished before it could pass through the condenser. In agreement with the experiments of Lind, no positive results were obtained with hydrogen–air mixtures. It is unfortunate that in the foregoing investigations no direct visual observations of the flame could be made while it was under the influence of the field. The gases were passed through the annular space between two metal cylinders between which a potential could be applied. The cooling effect of the wall must have been considerable in view of the small space (1.5 to 4 mm.) between the cylinders.

For some time we have been engaged in an investigation of the effects of an electric field on flames, and it is the purpose of this paper to explain briefly the method used and to make known some of the results obtained. In view of the fact that new equipment is being obtained for the production of steady high voltage, and for measuring voltage and ionization currents accurately, these results are preliminary in character.

[6] Kirkby and Haselfoot, *Phil. Mag.*, [6] 8, 471 (1904); de Muynck, *Acad. Roy. Belge*, 901 (1907); Garner and Saunders, *Trans. Faraday Soc.*, 22, 281 (1926); Saunders, *ibid.*, 23, 242, 256 (1927); Saunders and Sato, *ibid.*, 23, 248 (1927).

[7] Saha, *Phil. Mag.*, 40, 478, 809 (1920); 41, 267 (1921); 46, 534 (1923); *Proc. Roy. Soc.* (London), A99, 135 (1921).

[8] F. Haber, *Sitzb. preuss. Akad. Wiss.*, No. 11, 162 (1929).

[9] Lid, *J. Phys. Chem.*, 28, 57 (1924) (H_2 and O_2); Wendt and Grimm, *Ind. Eng. Chem.*, *16*, 890 (1924) (C_2H_2–air).

[10] Malinowski, *J. chim. phys.*, *21*, 469 (1924).

[11] Bernackyj and Retaniw, *Ukv. Physik Abhand*, Vol. II, No. 1, p. 9 (Dec., 1928).

[12] Malinowski and Lawrow, *Z. Physik*, 59, *690* (1930).

Method

There are two ways in which an electric field may be applied: (1) longitudinally—that is, in the direction of the flow of gas; and (2) transversely — that is, across the gas stream. The longitudinal field method possesses certain advantages—namely, that the flame is not in contact with the electrodes and that possibly more information may be obtained concerning the role of ionized species by reversing the direction of the field. The first method was employed in these experiments.

Apparatus

To obtain a source of direct current, a transformer, synchronous rectifier, condensers and choke coil were arranged as in Fig. 1. The amount of ripple in the delivered potential was estimated to be about 5 to 8%. A synchronous rectifier is not entirely satisfactory because marked variations in potential sometimes occur; it served well, however, for these experiments. The potentials were measured by means of an electrostatic voltmeter. After considerable time had been spent on cell construction, a cell was finally adopted which was both durable and simple to construct. It consists (see Fig. 2) of a Pyrex glass tube of 1 cm. inside diameter into which two electrodes were placed 1 cm. apart. The electrodes consist of 80-mesh nichrome wire gauze bent by means of a special die into shape to fit the glass tube snugly. The outer edge of the electrodes was cemented to the glass tube by means of a porcelain cement, Insalute. The leads were attached firmly and brought out through side arms, in which they were sealed with wax. Ignition of the gas–air mixtures was accomplished by sparking (with a spark coil) across the electrodes.

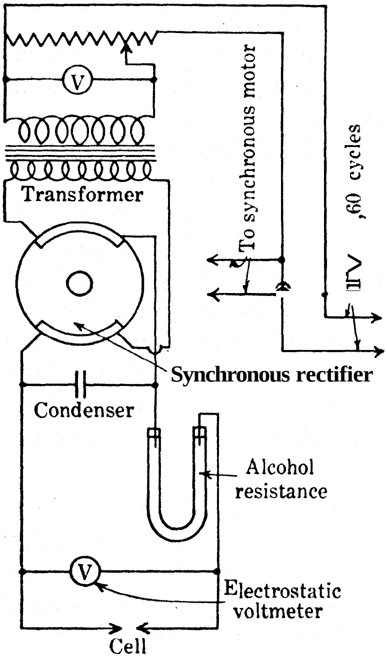

Fig. 1.—Apparatus used in experiments to determine the effect of electric field on flames.

Of the gases used, methane, ethane, ethylene, propane, propylene, butane, isobutane and butylene were obtained reasonably pure in tanks. Pittsburgh natural gas was taken from the pipe line and carbon monoxide was prepared from sulfuric acid and formic acid.

Procedure

Air and the flammable gas were led separately through calibrated flowmeters in amounts to give the desired mixture. They were passed into a mixing chamber and thence through the cell. Samples of the mixture were withdrawn and analyzed as a check on the flowmeters. The rate of flow of the mixture was adjusted to just balance the velocity of propagation of the flame in the opposite direction. Under these conditions a steady, stationary conical flame could be made to burn midway between the electrodes. The potential was then applied and increased and the effects were noted. Experiments were performed with the downstream electrode both positive and negative. A blast of air was used to prevent the glass cell from melting. The products of combustion were led to the open through a wide tube.

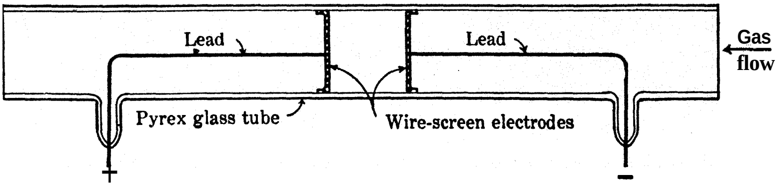

Fig. 2.—Diagram of cell used for confining a flame and applying an electric field.

Observations

The phenomenon observed, which is quite general for all the mixtures investigated, is that on application of the electric field the flame is invariably pulled toward that electrode which is negatively charged. Figure **3** shows this photographically. The upper picture is illustrative of a steady stationary flame of isobutane and air. The center picture shows the effect on the same flame on applying a field with the right-hand (upstream) electrode negatively charged. The lower picture shows the effect when the left-hand (downstream) electrode is negatively charged. This indicates that *the flame moves in the direction of positive ion flow.* It follows that the propagation of flame is *speeded up* if the upstream electrode is negatively charged and *slowed down* if the downstream electrode is negatively charged. Upon removing the electric field the flame returns to its original position in the tube.

If the potential applied is increased to a certain value, depending on the gas mixture, the flame may be extinguished. Depending on the direction of the field the phenomena observed are different. With the downstream electrode negatively charged, the flame is pulled toward this electrode as a body without much spreading. It undergoes intense oscillatory motions. Sometimes, when the potential is high enough, an occasional spark passes between the upstream (positive) electrode and the flame front. As the flame nears the negative electrode (with increasing potential) it becomes decidedly weak and unstable and then disappears. It is not possible to decide whether the flame is pulled through the wire-gauze electrode through which it is unable to propagate, or whether it is extinguished near the electrode accompanying the removal of charged species. With the upstream electrode negatively charged, the flame having been drawn toward this electrode spreads out somewhat, undergoes vibrations and takes on a weak-like, fading-out appearance prior to its disappearance. Here there is no question that the extinguishing of the flame is in some way connected with the removal of charged species. For the sake of convenience we shall arbitrarily denote the field as negative when the downstream electrode is negatively charged, and as positive when the upstream electrode is negatively charged.

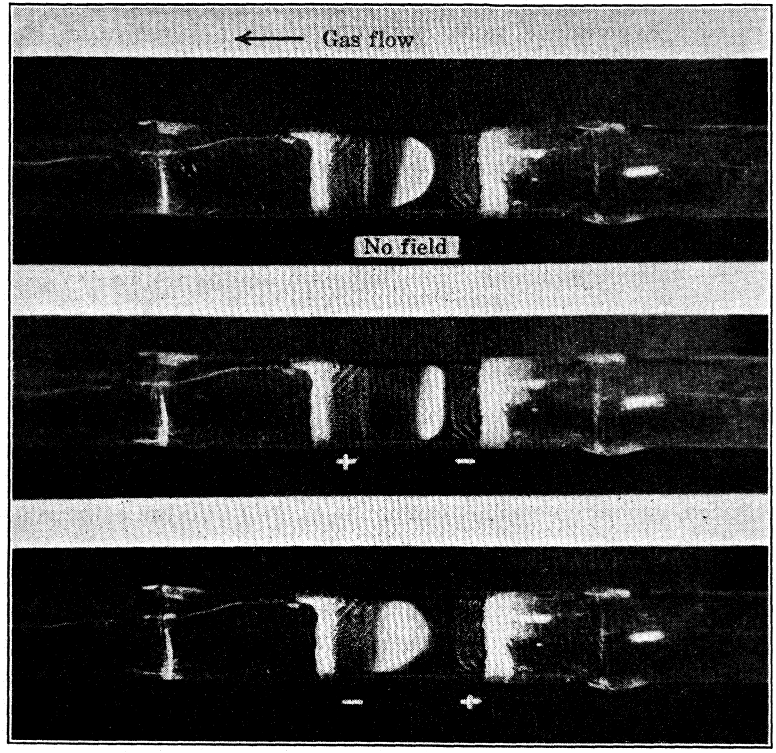

Fig. 3.—Photographs showing the effect of electric field on flames (natural size).

Table I summarizes the observations. Column 1 contains the flammable gas; column 2 the percentage of this gas mixed with air; column 3 the type of mixture—that is, whether it is richer or leaner in combustible gas than corresponds to a mixture in which gas and air are present in combining proportions. It should be noted that only in one or two cases was it

TABLE I

SUMMARY OF OBSERVATIONS

1	2	3	4	5	6
Combustible gas	Per cent. combustible	Type of mixture	Velocity of gases, cm./sec.	Voltage for extinguishing flame[a]	
				−Field	+Field
Pittsburgh natural gas	9.96	Rich	38	7500	1000
	10.33	Rich	41	6800	1700
	10.69	Rich	41	4500	1800
	6.46	Lean	42	7700	..
	8.43	Lean	38	6000	..
CH_4	11.61	Rich	29	9000	5000
	11.76	Rich	24	..	4300
	7.78	Lean	50	8000	..
C_2H_6	8.07	Rich	23	6500	2000
	7.96	Rich	51	6000	..
	4.77	Lean	48	6300	..
C_3H_8	4.90	Rich	39	5500	..
	2.97	Lean	31	7000	4250
	3.73	Lean	51	6500	4000
C_4H_{10}	4.43	Rich	19	3400	..
	4.43	Rich	38	4800	..
	2.7	Lean	40	5300	1800
	2.76	Lean	47	5200	3000
Iso C_4H_{10}	4.4	Rich	24	4300	..
	4.5	Rich	52	6000	..
	3.0	..[b]	53	4800	1400
	2.5	Lean	34	7000	1400
C_2H_4	10.74	Rich	28	1000	750
	10.8	Rich	51	5800	*ca.* 3000
	4.06	Lean	29.5	7700	*ca.* 2300
C_3H_6	7.33	Rich	25	4500	..
	4.2	..[b]	60	..	3600"
	3.3	Lean	26	7500	5000
C_4H_8	5.05	Rich	24	5000	..
	5.3	Rich	31	4300	..
	2.8	Lean	48	5000	*ca.* 1500
	3.0	Lean	*ca.* 50	6400	1600
CO	17.8	Lean	..	7000	..[d]
	22.3	Lean	..	6500	..[d]
C_2H_2	3.87	Lean	..	7000	..[e]

[a] The potentials for negative fields are usually considerably higher than those for positive fields. This is due to the fact that with a negative field the upstream portion of the cell which is free of flame is also practically free of ions and therefore highly resistant. With a positive field the downstream portion of the cell is free of flame but contains ions carried along by the moving gases, rendering this space conductive.

[b] Close to combining proportion mixture.

[c] Very unsteady flame prior to application of voltage

[d] Flows too high to be measured.

[e] Difficult to obtain steady flame with other mixtures.

possible to maintain a steady stationary flame between the electrodes with a mixture whose constituents were present in combining proportions. The flame of the latter mixture, which is close to one for which a maximum temperature and maximum flame speed are found, is usually extremely unsteady and very sensitive to small variations in composition.

Column 4 gives the velocity of flow of gases. These speeds may not correspond exactly to the horizontal speed of propagation of a flame in a 1-cm. tube measured in the usual way—namely, with stationary gases. Under the conditions of these experiments, turbulence is set up as a result of passage of the gases through the wire gauze. It becomes more pronounced with greater gas flows. Thus, it is possible to maintain stationary flames with quite different flows for the same percentage of combustible in the mixture.

Column 5 gives the potential at which the flame is extinguished with a negative field, and column 6 the potential at which the flame is extinguished with a positive field. Where dashes are indicated under positive field the flame was not extinguished with the highest voltage attainable (about **10,000** volts), although it was drawn toward the negative electrode, often violently, and set into intense vibration. At a somewhat lower voltage than this, sparks pass across the gap between one electrode and the flame. In a number of cases the flames were extinguished at voltages at which sparking occurred. However, this sparking was only intermittent (arising from gapping across the brushes of the synchronous rectifier). It was possible to observe that the flame was extinguished in a moment when the sparking ceased, in other words, when the applied potential was greatest. The voltages recorded were read just after the flame was extinguished.

Discussion of Observations

In many of the mixtures given in Table I the flame could be extinguished at practically every trial. In a few, the number of successful trials was from 7 to 8 out of 10. Where dashes are given under negative fields the flame could be extinguished only rarely, once or twice out of 10 trials. Dashes under positive fields, however, indicate no success in extinguishing the flame. Indeed, the phenomena are so easily reproducible that the experiment may be utilized for lecture demonstration with reasonable surety of success.

The results obtained by the longitudinal electric field method show:

1 The flames of rich mixtures of Pittsburgh natural gas (which is mainly CH_4 and C_2H_6), CH_4 and C_2H_6 are extinguished with positive fields; the flames of lean mixtures of these gases cannot be extinguished with positive fields.

2. The flames of lean mixtures of C_3H_8, C_4H_{10}, iso-C_4H_{10}, C_3H_6 and C_4H_8 are extinguished with positive fields; the flames of rich mixtures of these gases cannot be extinguished with positive fields.

3. The flames of rich or lean mixtures of all these hydrocarbon gases and in addition CO and C_2H_2, can be extinguished with negative fields. (It was found impossible to maintain a steady flame with rich mixtures of CO and C_2H_2 under these experimental conditions.)

The observed increase and decrease in the speed of propagation of flame may be linked with a greater or smaller concentration of ions. With a positive field in which an increase in velocity of flame propagation occurs, the ion concentration is greater than with a negative field in which a decrease in velocity is observed, because the field draws back into the flame ions which otherwise would have been carried downstream by the moving gases. An experiment by Malinowski[10] lends support to this view. He found that the ionic current was greater in the faster than in the slower moving portions of an oscillating non-stationary flame. If ion concentration governs flame speed, then, because the latter is directly related to the temperature of a flame, it follows that the temperature of a flame should be markedly affected by an electric field.

Several important questions arise. (1) Is the function of the ions and electrons to activate unburned molecules in the fresh gases and so raise them to the reaction threshold? (2) Is the formation of ions and electrons a result of collisions of the second kind between highly energized products of the reaction and molecules possessing low-ionizing potentials in the Haber sense? *(3)* Is the removal of positive ions the only requisite for extinguishing a flame, or are active molecules clustered around them and also drawn away from the reaction zone? At the present time these questions cannot be answered satisfactorily. It is evident, however, in the light of these experiments, that the positive ion plays an important part in the maintenance of flames.

Knowledge of the current–voltage characteristics would throw much light on the nature of flame processes. This we hope to determine with new equipment which we are designing.

Mention should be made of some results by Thornton.[13] He observed that while the flame of a 7% methane–air mixture (lean mixture) was speeded up in a transverse field, there was no effect on a 9.5% mixture (combining proportions). On the other hand, Malinowski and Lawrow[12] observed a marked slowing up of a 15% methane–air mixture (rich mixture). It has been shown above by the longitudinal field method that the flame can be speeded up or slowed down in a rich or lean mixture, depending merely on the direction of the field.

Some further experiments employing a tranverse field may be mentioned. Using a duplicate of Thornton's cell it was found, in agreement with him, that with a 7% methane–air mixture the propagation of flame could be speeded up very much (2 to 3 times) if the flame was moving originally in

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[13] Thornton, *Phil.* Mag., 9, 260 (1930).

the direction of oncoming unburned gases. If the velocity of the same mixture was adjusted so as to produce a stationary flame, the propagation was slowed down—that is, the flame moved in the direction of flow of gases. The strength of the field was below that which would extinguish the flame.

Likewise in rich mixtures, such as Malinowski used, propagation could be speeded up or slowed down under the same conditions mentioned above. Rich or lean butane–air mixtures showed the same effects. Acceleration of the flame was never observed, however, in a long rectangular cell two sides of which were of metal and two sides of transparent mica. In this cell, whatever the conditions, the speed of propagation was decreased by the transverse field.

These results clear up the apparent differences between the results of Thornton and Malinowski. The former worked with a flame in motion and the latter with an almost stationary flame or one moving slowly in the same direction as the gases. It is believed that these totally different effects are due to a difference in the shape of the flame fronts when the flame is in movement and when it is stationary,[14] which probably results in the positive ions being drawn on the one hand more to the upstream side and on the other hand the downstream side of the flame' front.

As the proof of this paper was being read, attention was drawn to a recent publication by Guénault and Wheeler.[15] These authors show pictures of the distortion of flames under the influence of an electric field and reach the same conclusion as the writer—namely, that the flame moves in the direction of the positive ion flow.

Acknowledgment. The writer takes pleasure in acknowledging the assistance of Harold J. Muendel, coöperative research fellow, Carnegie Institute of Technology.

Summary

The effects of an electric field on the flames of ten hydrocarbon–air and carbon monoxide–air mixtures were investigated. The field was applied in the same direction as the moving gas between fine wire-gauze electrodes placed on either side of a stationary flame confined in a Pyrex glass tube. It is found that the flame is invariably pulled toward that electrode which is negatively charged. Photographs of this effect are shown. These indicate that the flame moves in the direction of positive ion flow, and it follows that the propagation of flame is speeded up or slowed down depending on the direction of the electric field. With appropriate field direction and strength, the flames of all the mixtures could be extinguished. The results show that:

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[14] See Mason and Wheeler, *J. Chem. Soc.*, 1227 (1920), and Thornton, Ref. 13.

[15] Guénault and Wheeler, *J. Chem. Soc.*, 195 (1931).

1. The flames of rich mixtures of Pittsburgh natural gas, CH_4 and C_2H_6, are extinguished when the upstream electrode is negatively charged; the flames of lean mixtures of these gases cannot be extinguished with this direction of the field.
2. The flames of lean mixtures of C_3H_8, C_4H_{10}, iso-C_4H_{10}, C_3H_6 and C_4H_8 are extinguished when the upstream electrode is negatively charged; the flames of rich mixtures of these gases cannot be extinguished with this direction of the field.
3. The flames of rich or lean mixtures of all the above hydrocarbon gases and in addition lean mixtures of C_2H_2 and CO are extinguished when the downstream electrode is negatively charged.
4. Certain effects with a tranverse field are cleared up.

A brief discussion of the results is given. It is concluded that the positive ion plays an important role in the maintenance of flames.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

SONIC STUDIES OF THE PHYSICAL PROPERTIES OF LIQUIDS. II. THE VELOCITY OF SOUND IN SOLUTIONS OF CERTAIN ALKALI HALIDES AND THEIR COMPRESSIBILITIES

BY EGBERT B. FREYER[1]

RECEIVED JANUARY 29, 1931 PUBLISHED APRIL 6, 1931

In a previous paper[2] the velocities of sound in a number of organic liquids were reported. The measurements were made according to the method of Hubbard and Loomis,[3] and from the data so obtained, with the aid of other data, the adiabatic compressibilities, and in some cases also the isothermal compressibilities, were calculated. For the details of the method reference must be made to the earlier papers. It shall suffice here to mention that the high frequency or supersonic waves were generated by the piezo action of a quartz disk. For producing the high frequency alternating field a common type of vacuum tube oscillator was employed, and the positions and separation of nodes were indicated by abrupt changes of frequency. A secondary quartz controlled oscillator served to fix the frequency at resonance, and using a double heterodyne method the position of nodes as read from a micrometer screw could be determined to within

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[1] From the dissertation submitted by Egbert B. Freyer in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

[2] Freyer, Hubbard and Andrews, THIS JOURNAL, 51, 759 (1929).

[3] Hubbard and Loomis, Phil. Mag., [7] 5, 1177 (1928).

0.002 mm. The following equation relates the velocity of sound V in a liquid to its adiabatic compressibility β_ϕ, and density ρ

$$\beta_\phi = \frac{1}{V^2\rho}$$

The isothermal compressibility β_T may be calculated from β_ϕ by means of the thermodynamic relation

$$\beta_T = \beta_\phi + \frac{\alpha^2 T}{JC_p\rho}$$

where α is the coefficient of thermal expansion, C_p the specific heat at constant pressure at absolute temperature T, and J is the mechanical equivalent of heat. These equations were used to calculate the data presented in this paper.

Solutions of Alkali Halides

Since Hubbard and Loomis[3] had observed an apparently anomalous behavior of sodium iodide solutions (compared to those of potassium chloride and sodium chloride) in respect to the course of their curves of velocity of sound against temperature, it was considered desirable to study rather closely the velocity of sound in the chlorides, iodides and bromides of sodium and potassium.

The samples of the salts used were of the "Baker's C. P. Analyzed" grade, the purity of these being sufficiently high for the precision of this investigation. Considering, for example, that the most likely impurity in a given halide of potassium would be the same halide of sodium, it is evident from Fig. 2 that a trace of one salt in the other would have only a very slight effect on the velocity of sound. As much as a tenth of a per cent. of potassium chloride in sodium chloride would lower the velocity of sound in a solution only 0.05 m./sec., and the effect diminishes in the order Cl > Br > I. A precision greater than 1.0 m./sec. is not claimed for these measurements.

Results

In Table I are recorded the same quantities calculated from the velocity of sound as were reported for the organic liquids, except that here the compressibilities, etc., are given as a function of the weight per cent. of salt in solution. The data are for 20°. The density values are from the "International Critical Tables." The coefficients of expansion were calculated from density tables. The specific heat data were taken from the Landolt–Bornstein "Tabellen."

Table II shows (a) the velocity of sound and adiabatic compressibility as a function of temperature for concentrated solutions of the salts, and (b) the velocity of sound alone as a function of both temperature and concentration in the case of the iodides. All these data were taken from smooth curves drawn through the experimental points found by the author

TABLE I

DATA FOR SALT SOLUTIONS

Concn., %	Velocity of sound, m/sec.	ρ	β_ϕ	α	C_p	β_T	C_p/C_v	$\beta_{\phi_0} - \beta_\phi$
				NaCl				
1	1497.0	1.0053	45.00 $\times 10^{-6}$	0.0'3223	0.986	45.36 X 10^{-6}	1.008	1.10
6	1554.5	1.0413	40.28	283	.931	40.86	1.014	5.82
10	1600.5	1.0707	36.96	344	.892	37.84	1,024	9.14
16	1673.0	1.1162	32.45	396	.844	33.62	1.036	13.65
20	1722.5	1.1478	29.76	423	.818	31.11	1.045	16.34
24	1771.5	1.1804	27.36	449	.794	28.89	1.050	18.74
				NaBr				
1	1487	1.0060	45.56	0.03218	.987	45.90	1.007	0.58
6	1503	1.0462	42.89	276	.932	43.45	1.013	3.21
10	1517	1.0803	40.77	320	.889	41.52	1.018	5.33
16	1541	1.1352	37.60	383	.827	35.70	1.029	8.50
20	1558	1.1745	35.55	421	.788	36.91	1.038	10.55
30	1605	1.2841	30.64	505	.697	32.67	1.066	15.46
				NaI				
6	1483	1.0463	44.05	0.0_3269	.936	44.57	1.012	2.05
10	1483	1.0808	42.64	308	.894	43.33	1.016	3.46
20	1486.5	1.1769	38.97	400	.788	40.19	1.031	7.13
30	1494	1.2907	35.18	477	.688	36.99	1.051	10.92
40	1509	1.4271	31.21	537	.592	33.63	1.078	14.89
45	1524	1.5062	28.97	561	.550	31.66	1.093	17.13
				KCl				
1	1492	1.0046	45.32 X 10^{-6}	0.0_3215	.985	45.65 X 10^{-6}	1.007	0.78
6	1530	1.0369	41.76	258	.923	42.25	1.012	4.34
10	1560	1.0633	39.17	287	.877	39.80	1.016	6.93
16	1604	1.1043	35.67	324	,818	36.50	1.023	10.43
20	1633	1.1328	33.55	345	.784	34.50	1.028	12.55
24	1662.5	1.1628	31.55	365	.753	32.63	1.034	14.55
				KBr				
1	1486.5	1.0054	45.74	0.03215	.987	46.07	1.007	0.36
6	1495.0	1.0426	43.50	260	.927	44.00	1.011	2.60
10	1502.5	1.0740	41.80	292	.880	42.44	1.015	4.30
20	1521.5	1.1601	37.74	360	.767	38.77	1.027	8.36
30	1545.5	1.2593	33.70	408	.658	35.13	1.042	12.40
40	1573.0	1.3746	29.80	433	.553*	31.55	1.059	16.30
				KI				
6	1480.5	1.0437	44.31	0.0_3257	.932	44.79	1.011	1.79
16	1475	1.1284	41.29	333	.819	42.14	1.021	4.81
30	1472	1.2712	36.80	441	.667	38.24	1.039	9.30
45	1477	1.4672	31.67	462	.512*	33.70	1.063	14.43

and by Hubbard and Loomis, plotted as shown in Figs. 1 and 2. From the first it is seen that increasing the concentration of salt increases the ve-

TABLE II

EXPERIMENTAL DATA

(a)

Temp., °C.	Velocity of sound, m./sec.	P	$\beta\phi$
	26% NaCl		
20	1796	1.1972	26.25×10^{-6}
25	1799	1.1944	-26.23
30	1801	1.1917	26.22
40	1802	1.1861	26.32
	30% NaBr		
15	1599	1.2870	30.80
20	1605	1.2841	30.64
25	1609	1.2811	30.56
30	1612	1.2780	30.53
40	1615	1.2718	30.56
50	1616	1.2654	30.67
	45% NaI		
10	1525	1.5146	28.77
20	1524	1.5062	28.97
30	1525	1.4980	29.09
40	1525	1.4897	29.26

Temp., °C.	Velocity of sound, m./sec.	ρ	$\beta\phi$
	20% KCl		
15	1623	1.1347	33.91
20	1633	1.1328	33.55
25	1641	1.1307	33.29
30	1649	1.1285	33.03
40	1661	1.1240	32.68
50	1669	1.1192	32.51
	30% KBr		
20	1545.5	1.2593	33.70
25	1554	1.2566	33.40
30	1561	1.2539	33.17
40	1571	1.2484	32.90
50	1576	1.2423	32.85
	30% KI		
10	1457	1.2762	37.42
20	1472	1.2712	36.80
30	1483.5	1.2658	36.38
40	1492	1.2600	36.14
50	1498.5	1.2537	36.01
60	1504	1.2472	35.93

(b)

Temp.,	KI				Pure	NaI				
°C.	**6%**	**15%**	**30%**	**45%**	***water***	**15%**	**30.5%**	**40%**	**45%**	**46.8%**
15	1465	1464	1465	1473	1467.5	1472	1488	1507	1525	1534
25	1495	1486	1478.5	1481	1498.1	1495	1500	1512	1525	1532
35	1516.5	1503	1488.5	1488	1520.6	1511.5	1508	1515	1525	1530
45	1530	1515	1495.5	1492						1528
55	1538	1522	1501							

locity of sound in solutions of sodium chloride, potassium chloride, sodium bromide and potassium bromide. In the case of potassium iodide the velocity decreases and passes through a minimum at about 37%, at 25, 35 and 45°, whereas at 15° the minimum occurs at 20% salt concentration. Considering sodium iodide, the minimum shifts to lower concentration as the temperature is lowered. An explanation of the general course of these curves will be given presently. In Fig. 2 is shown the change in the velocity of sound in solutions of varying concentration as the temperature changes. A characteristic of all the curves is the decrease in slope at a given temperature and a general flattening as the concentration increases. This tendency is least in the case of potassium chloride. The slope of the curve is zero for 45% sodium iodide and becomes negative at higher concentration. Figure 3 shows the lowering of the adiabatic compressibility produced by adding the various salts to water as a function of the quantity of salt added.

Discussion

Since the velocity of sound in a liquid is related to its density and adiabatic compressibility, we should be able to predict changes in the first quantity if we know how the other two vary. The general trend of the velocity of sound-concentration curves is accounted for as follows: the decreasing compressibility tends to increase the velocity, while the increasing density tends to lower it. The predominating effect obviously determines whether addition of salt shall increase or decrease the velocity of sound in the solution. These relations are clearly illustrated by the figures of the first two columns of Table III, where the fractional changes

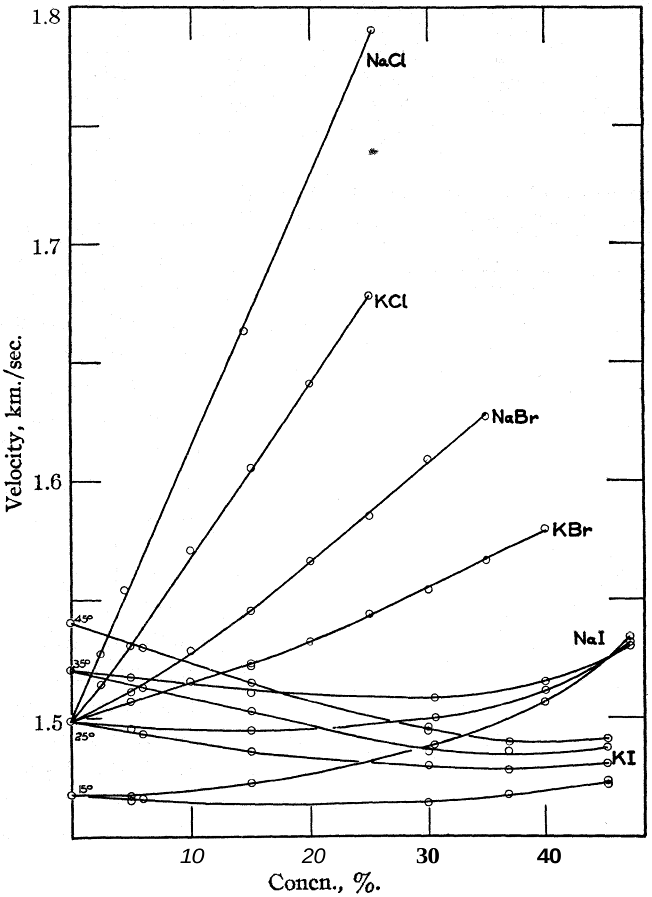

Fig. 1.

TABLE III

DATA FOR 10% SALT SOLUTIONS

	(a) $\frac{\beta\phi_0 - \beta\phi}{\beta\phi_0}$	(b) $\frac{\rho - \rho_0}{0.01\,\rho_0}$	(c) γ	(d) $\frac{(b)}{(c)}$	(e) Molecular weight
NaCl	0.198	7.07	0.64	11.1	58.5
KCl	.150	6.33	.58	10.9	74.6
NaBr	.116	8.03	.70	11.4	102.9
KBr	.093	7.39	.61	12.1	119.0
NaI	.075	8.09	.72	11.2	149.9
KI	.065	7.61	.67	11.4	166.0
LiCl		5.59	.93	6.0	
HCl		4.57	1.15	4.0	

in the compressibility and percentage density change due to adding 10% of each salt are recorded. In the case of sodium chloride the compressibility change greatly predominates and the velocity of sound increases relatively quite rapidly. · This predominance decreases in the order NaCl>KCl>NaBr>KBr. The density change has the greater influence in the case of sodium iodide and potassium iodide, and the velocity of sound in solutions of these salts accordingly decreases with concentration. The same reasoning evidently applies also to the curves of Fig. 1, except that here the velocity of sound change is determined by the effect of temperature on the compressibility and density.

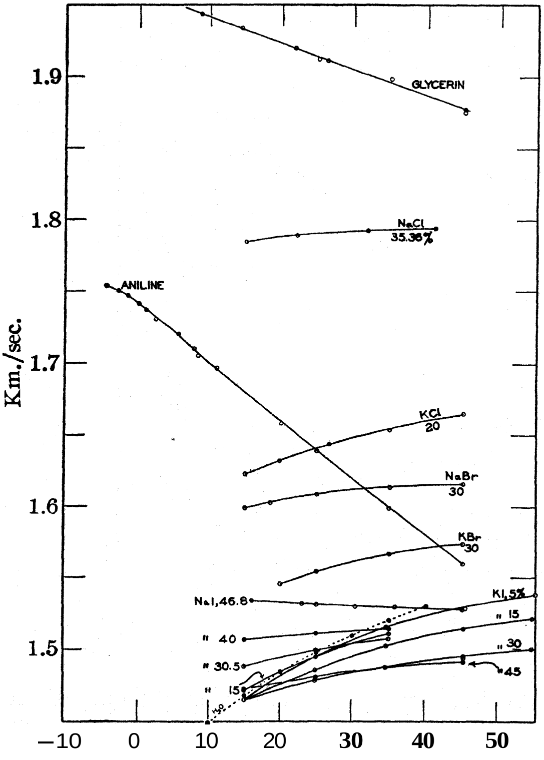

Fig. 2.

Figure 3 shows that a solution of each of the several salts has a lower compressibility than has the pure solvent, and that the lowering produced is greater the larger the amount of salt added. It seemed of interest to examine rather closely the specific effect of each salt at one concentration.

To this end a number of properties of the salts and of their ions were sought in the literature, in the hope that a qualitative relation, at least, might be found between some of these properties and the effect of the ions on the compressibility of their solution. The following question presents itself: what factors may be operative when a salt is added to water that might produce a compressibility change? First, it is conceivable that the presence of ions may change the condition of aggregation of the solvent molecules, *i. e.*, may shift the trihydrol–dihydrol–monohydrol equilibria. Second, it is known that ions concentrate solvent molecules in their immediate vicinity, this hydration being, in effect, a compression, and related to a volume change observed when the components are mixed. It seems a fairly remote possibility that the compressibility of a salt as measured for the solid should have an appreciable effect on that of its solution. The first two possibilities become one when we consider that any effect of the ions on the equilibria between the various hydrols would actually be brought about as a result of hydration. Now the compressibility of a substance decreases with increasing pressure or, simply, the more a substance is compressed the less it can be compressed. It should accordingly be expected that for a given concentration those solutions will have the lower compressibility whose ions are most hydrated, or, expressed in another way, the lowering of the compressibility produced when different salts are added to water should vary in the same order as the relative degrees of hydration of their ions. Thus Webb[4] has calculated the contraction of the solvent produced by ions of various radii.

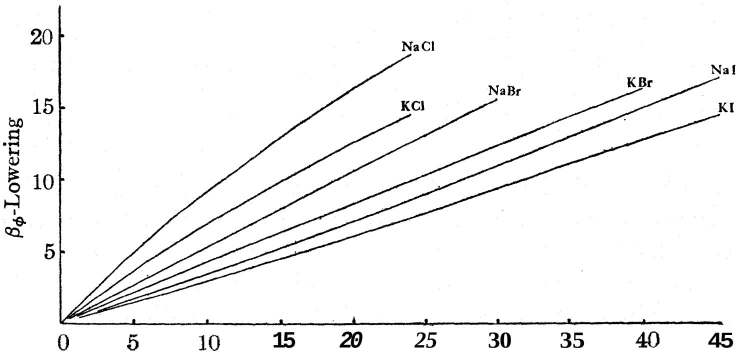

Fig. 3.

The figures in column two of Table IV represent the mean contraction produced by the two ions composing the salts which affect the fractional compressibility lowerings given in the first column. The assumption is made that this contraction effect is a measure of the relative mean degree

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[4] Webb, This Journal, **48**, 2598 (1926).

of hydration of the ions. The third column shows how nearly the compressibility change is proportional to the contraction. The mean ionic radii of the salts as calculated by Webb are given in the fourth column. It is to be noted that in the range considered, the contraction of the solvent is almost inversely proportional to the mean radii of the ions producing it. This is due to the greater intensity of the electric field about the ions of the low atomic number and small radii, resulting in a greater attraction of the water dipoles for the ions. This is the so-called electrostriction.

TABLE IV

DATA FOR 3 MOLAL SALT SOLUTIONS

	(a) $\frac{\beta\phi_0 - 84}{\beta\phi_0}$	(b) Mean relative contraction	$\frac{(b)}{(a)}$	Mean r, Å.
NaCl	0.129	10.7	83	1.87
NaBr	.124	10.2	83	1.95
NaI	.113	9.5	84	2.05
KCl	.116	9.5	82	2.05
KBr	.108	9.0	83	2.12
KI	.105	8.4	80	2.23

It would seem desirable, before concluding, to direct attention to one further observation. It is the approximate proportionality between the activity coefficients and percentage density changes due to equal weight percentages of the six salts in solution. This is shown in the last column of Table III. The data are for 10% solutions. The relation is seen to be not even approximate in the case of lithium chloride and hydrochloric acid. This is not surprising in view of the differences in properties usually observed between the elements of the first series of the periodic table and those of the other series. It was found also not to hold for salts of other valence types.

Summary

The velocity of sound in solutions of iodides, chlorides and bromides of sodium and potassium has been measured, using high frequencies and a resonance method of detecting nodes. The data cover nearly the entire concentration range for the various salts, and the temperature range 15 to 45°.

The adiabatic and isothermal compressibilities have been calculated for various concentrations at 20°. The adiabatic compressibilities have been calculated as a function of temperature for certain concentrated solutions of the salts.

It is shown that addition of salt lowers the adiabatic compressibility of the solutions, the lowering being quite different for equal percentages of the different salts, and much more nearly equal for equal molalities. In the latter case, the lowering is shown to be related to the contraction of the solvents and hence, presumably, to the hydration produced by the ions.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY, HARVARD SCHOOL OF PUBLIC HEALTH]

THE COLORIMETRIC DETERMINATION OF MINUTE AMOUNTS OF CADMIUM

BY LAWRENCE T. FAIRHALL AND LEON PRODAN

RECEIVED JANUARY 30, 1931 PUBLISHED APRIL 6, 1931

Cadmium is becoming increasingly an industrial hazard both in the primary smelting of ore and in such secondary uses as cadmium plating. The need for an accurate method for the determination of minute amounts of the metal is apparent both in the analysis of ores and in toxicological investigation of the substance. Although many methods for the micro scopical detection of cadmium have been developed, none of these is particularly applicable to quantitative use. The blue color which is developed when resorcinol is added to solutions of cadmium salts[1] is far less intense than that developed by zinc, is subject to vagaries and is seriously affected by other metals which yield the same color. Breyer[2] determined small amounts of cadmium in the dry way by volatilizing cadmium and measuring the depth of yellow color of the sulfide deposited on a glass tube. The most promising method is that of Hessel,[3] who employed the yellow color of the sulfide in solutions as a means of determining cadmium quantitatively in amounts of 2 to 10 milligrams in organic material. These various methods and several of the microscopic methods were investigated in an attempt to develop a method for cadmium analysis, accurate for small quantities and particularly in organic material.

Experimental

In the initial experiments it was found that extremely dilute solutions of cadmium salts, which under ordinary light develop only a faintly yellow coloration with hydrogen sulfide water, give a pronounced bright yellow appearance under a quartz mercury vapor lamp. In concentrations of less than 0.1 mg./50 cc. of cadmium, differences in the yellow color of the sulfide become indistinguishable in ordinary light, while under the mercury arc the yellow color is perceptible in concentrations as low as 0.01 mg./50 cc., so that differentiation may be made with experience between solutions of this volume varying but 0.01 mg. of cadmium in amount. If we assume a lower limit of twice this value, however, that is, of 0.02 mg./50 cc., this represents a delicacy of 1:2,500,000, whereas Hessel found with his method a delicacy of but 1:70,000.

Since cadmium and its salts are so volatile, ashing in the ordinary way is out of the question. Nitric acid ashing with the addition of a small

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[1] M. Lavoye, *J. Pharm. Belg.*, 3, 889 (1921).

[2] F. G. Breyer, *Comm. 8th* Inter. *Cong. Applied Chem., 25,* 1–5 (1912).

[3] G. Hessel, *Biochem. Z.*, 177, *146* (1926).

amount of sulfuric acid gives good results and in the case of animal tissues is most conveniently effected by slow oxidation in conical beakers at a low heat on an electric hot-plate. As cadmium sulfide is much more insoluble in acid than zinc sulfide, it is possible to separate the two readily when the zinc is not present in greater amount than that found in animal tissues. In order to insure complete separation of the cadmium as sulfide, copper may be added as an entraining medium. Copper was chosen because it is normally present in animal tissues and because the coloration of cadmium sulfide may be produced in the presence of copper without interference merely by the addition of potassium cyanide. The disagreeable tendency of cadmium sulfide to pass into the colloidal condition when it is washed is readily overcome by the addition of a drop of 5% aluminum chloride solution in the initial stage of separation.

Using the method outlined below, various analyses were made of organic material to which known amounts of cadmium had been added. Cadmium in amounts varying from 0.40 to 1.00 mg. was added in each case to 100 g. of muscle and the material oxidized. The cadmium was separated and read as the sulfide, comparison being made with cadmium standards prepared in an exactly similar manner. Readings were made by two observers on separate aliquot portions of the separated cadmium chloride obtained in the course of analysis. The results are shown in the following table. The error in these analyses ranged from zero to 0.09 mg. and averaged 0.04 mg.

TABLE I

RESULTS OF EXPERIMENTS

Number	Amount present, mg. of Cd	Readings			Amount found, mg. of Cd	Error
		P.		F.		
1	0.50	0.10	0.08	0.08	0.43	0.07
2	1.00	.20	.15	.20	.91	.09
3	1.00	.20	.17	.20	.95	.05
4	1.00	.20	.17	.18	.91	.09
5	0.40	.08	.08	.08	.40	.00
6	.60	.10	.11	.11	.53	.07
7	.50	.10	.08	.10	.47	.03
8	.80	.15	.15	.15	.75	.05
9	1.00	.20	.18	.19	.95	.05
10	1.00	.20	.18	.20	.97	.03
11	0.90	.18	.13	.18	.81	.09
12	.80	.16	.14	.17	.79	.01
13	.50	.09	.08	.10	.45	05
14	1.00	.20	.15	.20	.92	.08
15	1.00	.20	.15	.20	.92	.08
16	0.50	.10	.09	.10	.49	.01
17	1.00	.20	.20	.20	1.00	.00
18	1.00	.20	.20	.20	1.00	.00
19	1.00	.20	.20	.20	1.00	.00
20	1 00	.20	.20	.20	1.00	.00
					Average	0.04

Method of Analysis

Add sufficient concentrated nitric acid to the organic material to cover it and heat it very gently at first. After the solid material has dissolved, add 10 cc. of concentrated sulfuric acid and occasionally add small amounts of nitric acid until oxidation is complete and then heat until fumes of sulfur trioxide are freely given off. Dilute to 75 cc. and add the equivalent of 0.5 mg. of copper and 2 g. of sodium citrate. Neutralize the acid solution for the first precipitation with ammonia (rather than potassium hydroxide, as this avoids precipitation of potassium sulfate from the cooling solution) and adjust the concentration of hydrogen ion to approximately 10^{-3} by means of the indicators thymol blue and brom chlor phenol blue. Pass hydrogen sulfide into the resulting solution for five to ten minutes, add one drop of 5% aluminum chloride solution and allow the solution to stand for six to twelve hours. Filter, dissolve the precipitate in nitric acid and hydrochloric acid and carefully evaporate to dryness. Repeat the precipitation as sulfide twice more, omitting the addition of sodium citrate the last time and adjusting the hydrogen-ion concentration to 10^{-2} by means of dilute potassium hydroxide. Carefully evaporate the final solution of chloride to dryness, dissolve it in water and make up to a convenient exact volume in a volumetric flask. An aliquot portion of this solution is used in a Nessler tube for the final reading. To each tube add five drops of 10% potassium cyanide, distilled water and finally 5 cc. of hydrogen sulfide water. Mix thoroughly and compare under a flood of ultraviolet light with standards similarly prepared. The solution should exhibit a bright, clear yellow color under the mercury arc. Dark or turbid solutions usually indicate incomplete removal of iron. Traces of lead although not usually present in animal tissues are usually found in the reagents and must be removed.[4] The reagents are usually free from cadmium. The comparison tubes and the standard tubes should be prepared at the same time, as there is a notable deepening in tone when they are allowed to stand overnight. In doubtful cases, however, it is sometimes advantageous to allow the tubes to stand for a few hours before reading.

Conclusion

A colorimetric method for the determination of minute amounts of cadmium is described in which advantage is taken of the intensification of color of the sulfide under ultraviolet rays. A sensitivity of 1:2,500,000 is thus obtained and an accuracy attained of 4% in the analysis of material containing from 0.40 to 1.00 mg. of cadmium in 100 g. of organic material.

BOSTON, MASSACHUSETTS

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[4] L. T. Fairhall, *J. Biol. Chem.*, **57**, 461 (1923).

[Contribution from the Frick Chemical Laboratory of Princeton University]

THE ROLE PLAYED BY ADSORBED GASES IN INITIATING REACTION CHAINS: THE COMBINATION OF HYDROGEN AND OXYGEN

By Hubert N. Alyea

Received February 4, 1931 Published April 6, 1931

Reaction chains initiated in the gas phase, and being broken upon collision with the walls of the containing vessels, have received considerable attention during the past few years. This paper presents a new type of chain mechanism: one in which chains are initiated on a catalytic wall surface, enter into the gas phase, and may eventually return to be broken at the walls.

An equivalent oxygen–hydrogen mixture at about 550° has been found by Thompson and Hinshelwood[1] to exhibit an extremely interesting phenomenon. Between the limits 10 to 100 mm. mercury pressure it explodes; outside these limits it does not. The variation of these limits with temperature is represented by the unbroken line in Fig. 1. At pressures greater than the upper explosion limit B–C a slow measurable reaction occurs, which we shall designate as "the non-explosive reaction." It will be our purpose to develop the evidence which shows that the non-explosive and the explosive reactions differ strikingly from each other, and that factors which accelerate the former retard the latter. A change of a few millimeters' pressure, and the one type of reaction is replaced by its opposing type. For this phenomenon a mechanism will be proposed which involves selective adsorption of gases on the walls of the containing vessel, initiation of chains from these adsorbed gases, and subsequent extension of reaction chains out into the gas phase. Finally it will be shown that such a mechanism can explain other reactions as well, such as the oxidation of carbon disulfide, carbon monoxide and the hydrocarbons.

Explosion Starts from the Walls.—We have been able to demonstrate this by a method described in detail elsewhere.[2] Two heated porcelain tubes 2 mm. in diameter, at right angles to each other, conducted streams of oxygen and of hydrogen, respectively, into a large iron chamber filled with nitrogen. The gases were pumped off continuously. Suitable devices permitted adjusting the streams so that they exactly crossed each other in an atmosphere of nitrogen, determining their maximum temperature at the point of coincidence within 1° with a thermocouple, and regulating the pressure of the streams by altering the total pressure in the chamber. Under these conditions oxygen and hydrogen were brought together in the absence of walls. An approximately isothermal run was

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[1] Thompson and Hinshelwood, Proc. Roy. *Soc.* (London), [A] 122, 610 (1929).

[2] Alyea and Haber, *Z. physik.* Chem., [B] 10, 193 (1930).

made by crossing the oxygen and hydrogen initially at 50 to 200 mm. pressure, and following visually through a window in the chamber, or thermally with a thermocouple poisoned to prevent catalytic action, any change which occurred upon lowering the pressure to 10 mm. of mercury. At all pressures the temperature of the crossed streams remained about 20° higher than that of each single stream. The broken-line curves, Fig. 1, represent the thermal observations of seventeen such runs. In none of them is there a sudden increase in temperature when the pressure of the gases has fallen to the region where explosion should be occurring. Moreover, there were never any visual indications that explosion had taken place. This means that in the absence of walls no explosion occurs.

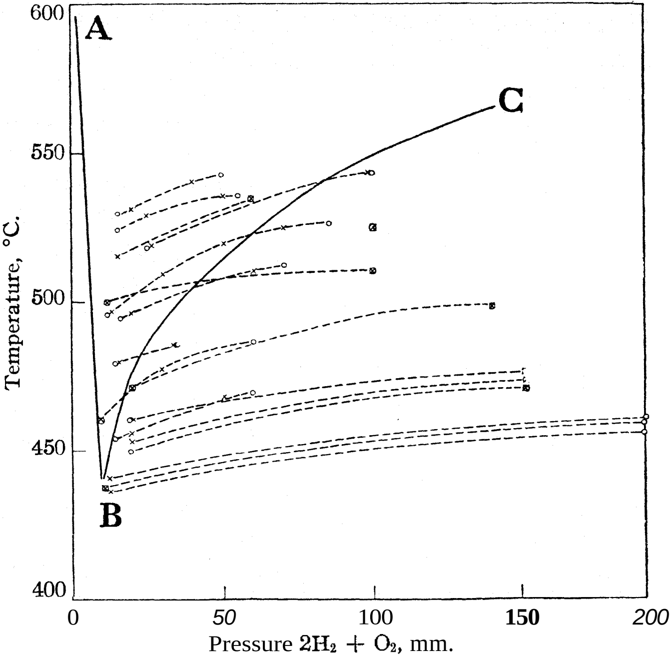


Fig. 1.

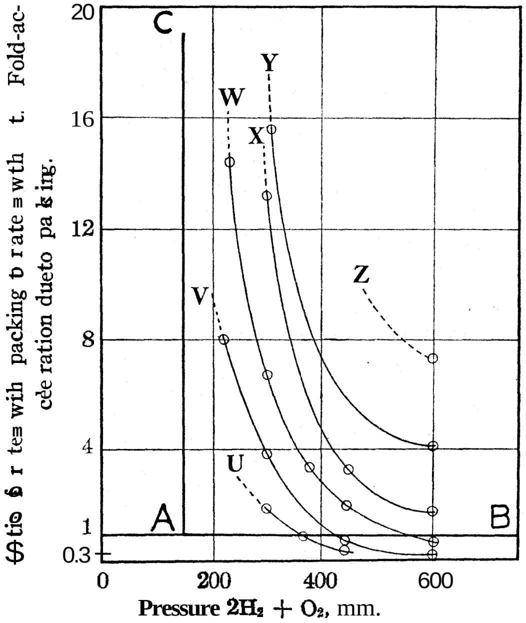
An artificial wall was then supplied: a quartz tube heated from within so that its surface was less than 520° was pushed into the gas stream at 530° and 35 mm., conditions where explosion should have occurred. As if lighted by a match, the gas exploded, and a visible sodium flame immediately appeared, extending from the quartz out into the gas in the direction in which the gas was flowing. The explosion continued until the quartz tube was removed from the gas stream. This could be repeated at will.

These facts clearly indicate that the explosion originates on the walls, and does not take place in their absence.

Unfortunately our experimental method does not give an equivalent oxygen–hydrogen mixture, but instead a portion of the crossed streams contains oxygen-rich mixtures which will explode even at pressures much above the upper explosion limit. This makes it impossible to identify the upper explosion pressure by the use of the quartz rod.

Effect of Different Surfaces.—Rods of glass, porcelain, copper, or iron, initiated explosion just as does quartz. **A** rod of aluminum, however, **was** without effect.

Effect of Packing.—The explosion limit is the same in quartz or porcelain vessels, unpacked or filled with crushed quartz or porcelain. This fact naturally led Hinshelwood,[1] and Semenoff and co-workers,[3] to believe the reaction to be homogeneous. The experiments described above, and the pretreatment experiments given below, at once disprove the homogeneous mechanisms, which they have postulated, for sudden explosion of oxygen–hydrogen mixtures, and warn against presenting such data as absolute proofs of homogeneity of reaction henceforth.



U, 576°; V, 569°; W, 559°; X, 549°; Y, 529°; Z, 506°.

Fig. 2.—The explosive region lies at pressures below AC. Values below AB indicate that packing retards reaction.

The non-explosive reaction, on the other hand, is extremely sensitive to the amount of surface present. Hinshelwood and co-workers early data[4] show that at pressures immediately above the upper explosion limit, the non-explosive reaction is accelerated by filling the vessel with bits of porcelain or silica. It must be pointed out that the retardation due to packing claimed by these authors applies only to their high pressure data; at pressures immediately above the explosion limit, packing accelerated, not retarded. This becomes obvious when their results are plotted as in Fig. 2, showing the packing

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[3] **Kopp, Kowalsky, Sagulin and Semenoff,** *Z. physik. Chem.*, **[B] 6,** 307 (1930).

[4] **Hinshelwood and Thompson,** *Proc.* **Roy.** *Soc.* **(London), [A]** 118, **170** (1928); **Gibson and Hinshelwood,** *ibid.*, **[A]** 119, 591 (1928).

effect at different temperatures. In a second paper,' however, they present data where, under comparable extent and particle size of packing material, it appears that packing tremendously retards reaction (Table I).

TABLE I

REACTION RATE DATA

Oxygen–hydrogen pressure, 555°, mm.	Ratio of rates with packing to rates without Early publications		Later publication
600	0.7	0.9	0.08
300	6.7	8.5	.056

The reason for this discrepancy between their early and later results no doubt lies in differences in the washing process or previous history of their packing material. Pease[5] found that a slight change in the nature of the glass walls, such as is obtained by washing the walls with a solution of potassium chloride, slows down the reaction several thousand fold. This is because the number of chains started is fewer, and the chain-breaking efficiency is increased, on the coated wall, as the work of Taylor and Lavin[6] on combination of hydroxyl radicals and hydrogen atoms on various surfaces amply confirms.

Effect of the Hydrogen–Oxygen Ratio.—Increasing the ratio accelerates the non-explosive, but is unfavorable to the explosive, reaction. The latter is demonstrated in Thompson and Hinshelwood's results in the first two columns of Table II, where in hydrogen-rich mixtures one must exhaust to lower total pressures before explosion will occur.

TABLE II

REACTION RATE DATA

H_2–O_2 ratio	Mixture explodes below (mm. Hg) Pressure $2H_2 + O_2$	Pressure H_2
0.5	129	43
0.67	115	46
1.0	97	49
2.0	99	66
3.0	83	62
4.0	68	56

Attention is directed especially to our calculation in the last column, where it is evident that the hydrogen pressure at which explosion sets in is fairly constant, irrespective of the hydrogen-oxygen ratio.

Pretreatment of the Walls.—Bone and Wheeler[7] showed that porcelain walls around 500° adsorbed large quantities of hydrogen, but no oxygen. Analogously, when walls were preexposed to hydrogen for some hours, subsequently admitted oxy-hydrogen gas reacted much faster. The surface activity was proportional to the length of pretreatment. Preëxpo-

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[5] Pease, THIS JOURNAL, 52, 5106 (1930).

[6] Taylor and Lavin, *ibid.*, 52, 1910 (1930).

[7] Bone and Wheeler, *Phil. Trans.*, [A] 206, 1 (1906).

sure to oxygen had no effect. It is striking that the increased activity of the surface due to hydrogen pretreatment was still manifest after the walls had been exposed continuously to the oxy-hydrogen mixtures for two hours, i. e., their reaction rate continued to be greater than normal.

For the explosive reaction we have found the reverse is true.[2] Ten liters per hour, measured at N. T. P., of oxy-hydrogen gas were passed through a porcelain reaction tubing 30 cm. long and 2 mm. in diameter heated at 550° and leading into the large partially evacuated chamber described above. Regulating the pressure in the chamber controls the pressure in the porcelain tube. Normally, if the gas is below 60 mm. pressure it explodes and burns at the mouth of the porcelain tubing; above this it ceases to burn, thus identifying itself with the upper explosion limit discovered by Thompson and Hinshelwood. Procedure was then varied: hydrogen was first passed through the heated tubing at 40 mm. pressure; this was followed by oxy-hydrogen gas at 200 mm., upon lowering the pressure of which, no explosion occurred. Conversely, pretreatment with oxygen seems to favor explosion. A series of consecutive runs carried out in one tubing, Table III, confirm this. Here is evidence that three minutes

TABLE III

DATA OF CONSECUTIVE RUNS

Consecutive pretreatments at 40 mm. with	Time of pretreatment in minutes	On withdrawing $2H_2 + O_2$ gas from 200 to 40 mm. it explodes at
$H_2 + O_2$	2	60 mm.
	2	50
	2	55
	2	70
H_2	5	No explosion
H_2	2	No explosion
O_2	2	70
O_2	3	65
O_2	1	90
O_2	1	60
$H_2 + O_2$	1	50
$H_2 + O_2$	2	50
H_2	3	No explosion
H_2	2	No explosion
H_2	1	No explosion
O_2	5	145
O_2	2	120
O_2	2	60
$H_2 + O_2$	1	70
H_2	6	No explosion
H_2	1	No explosion
O_2	0.5	No explosion
O_2	1.0	110

or longer of hydrogen pretreatment prevents explosion, and that this is counteracted by longer than thirty seconds oxygen pretreatment. We might add that oxy-hydrogen gas may be passed over the hydrogen pretreated surface for several minutes without normal explosion occurring. Four other tubes yielded the same qualitative results, although they required varying lengths of hydrogen pretreatment, up to fifteen minutes, to prevent the explosion. It can be seen in Table III that not even the normal explosion limit could be evaluated accurately.

The results on pretreatment, and the retarding influence of excess hydrogen, make it clear why Thompson and Hinshelwood found that at 550° hydrogen exploded upon streaming into oxygen at 135 mm. or less while oxygen did not explode upon admission to hydrogen unless the pressure of the latter was lower than 84 mm.

Effect of Steam.—Gibson and Hinshelwood[4] found that the addition of 40% of steam to the oxy-hydrogen mixture speeded up the non-explosive reaction six-fold. That explosion, on the other hand, is completely prevented under these conditions is seen in Table IV. Here our calculations on a few typical measurements by Hinshelwood and co-workers show that the oxy-hydrogen pressure during the course of many of their non-explosive reactions fell into that low pressure region where explosion should have occurred. The steam formed has prevented explosion.

TABLE IV

EXPERIMENTS WITH STEAM

Bulb	Temp., °C.	Initial pressures H_2	O_2	P_{steam} preventing explosian at P_E	Should explode below P_E	Non-explosive reaction measd. down to P_{final}
Packed silica	648	200	129	120	150	86
Packed porcelain	582	150	75	46	155	112.5
Empty silica	567	80	51.5	4	126	71.5
Empty silica	549	403	212	356	82	46

P_E and P_{final} are pressures in millimeters from data by Hinshelwood and co-workers.

Effect of Inert Gases.—Nitrogen and argon act in the same way as steam, accelerating the non-explosive reaction, but preventing explosion,[3,8] since in the absence of inert gases the oxy-hydrogen mixture will explode at higher pressures than in their presence.

Discussion

It is quite certain that we are dealing with chain reactions in both the explosive and the slow reaction,[9] probably involving the mechanism suggested by Bonhoeffer and Haber

$$OH + H_2 = H_2O + H$$
$$H + O_2 + H_2 = H_2O + OH$$

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[8] Thompson, *Z. physik.* Chem., [B] 10, 280 (1930).

[9] See Farkas, Haber and Harteck, *Naturwiss.*, 18, 266 (1930).

It is clear that the wall breaks the chains by catalyzing the recombination or interaction of H and of OH.

The Non-Explosive Reaction.—But how does the wall initiate chains? The answer was suggested in our introduction: gases adsorbed on its surface release into the gas phase a supply of hydrogen atoms. Bone and Wheeler's results on adsorbed hydrogen were so important as to warrant repetition. Their results are confirmed in Table V and Fig. 3. A 500-cc. Pyrex vessel was filled with coarsely powdered new Pyrex tubing, and placed in an oven. Between each run the vessel was exhausted at 500° for about twenty hours with a Cenco oil pump. The greater part of the gas

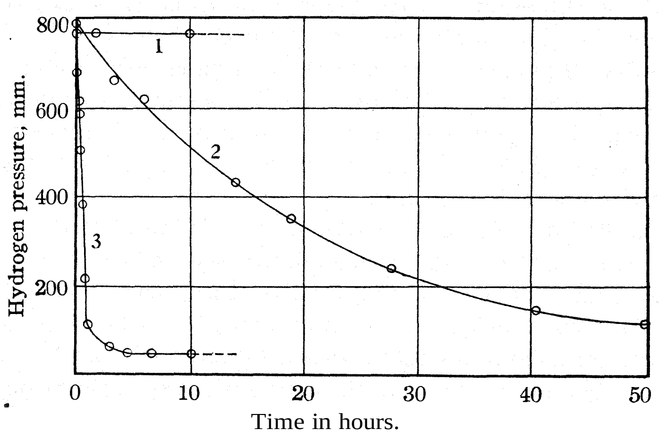


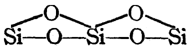
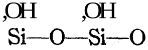
Fig. 3.—Curve 1 at 25°; Curve 2, at 480°; Curve 3, at 530°

TABLE V

RESULTS OF EXPERIMENTS

Time in minutes	Pressure of hydrogen, mm. Run I at 530°	Run II at 25°
0.00	700	760
0.50	617	
1	594	
2	553	
3	521	
4	494	
5	471	
10	383	
20	288	
30	227	759
60	113	
120	59	
240	49	
600	47	758
Final total volume of H_2 adsorbed reduced to N. T. P.	31 6 cc.	0 20

adsorbed could be pumped off and collected again at low pressures, although a small amount was consumed in reducing the Pyrex, which became darkened during the measurements. It is apparent that while no hydrogen was adsorbed at room temperatures, tremendous amounts were taken up at 500°. Oxygen under these conditions was not absorbed at either temperature.

Benton[10] observed the identical phenomenon for hydrogen on nickel. Such a type of curve can only be interpreted as meaning that *at the higher temperature hydrogen is adsorbed in an activated form which it is not at room temperature.* This is also substantiated in the pretreatment phenomena discussed above, where hydrogen being desorbed so slowly indicated a large heat of activation for the removal of the hydrogen. The silica surface  has now become possibly  $\overset{OH}{Si}-O-\overset{OH}{Si}-O$.

But we shall go one step further to state *that hydrogen in this form on glass is capable of performing reactions which it is unable to effect at room temperature.*[11] One possible reaction is

$$Si-OH + H_2 \longrightarrow Si-OH_2 + H$$

and by such a mechanism our chain reaction is initiated, the hydrogen atom being liberated into the gas phase.

Such a mechanism for the initiation of chains in the non-explosive reaction explains the phenomena discussed previously. Excess of hydrogen, pretreatment with hydrogen, increasing wall surface, would all accelerate the non-explosive reaction and such is found to be the case. The action of inert gases is possibly connected solely with the gas chains, not the initiating of them at the walls. Steam may act by changing the nature of the adsorbed gas layer[12] and breaking the gaseous reaction chains less easily than a dry surface.

In addition to giving us a satisfactory explanation for the hydrogen–oxygen reaction, this idea clarifies numerous other reactions. Polyakov,[13] passing hydrogen over palladium at 400° obtained an active form of hydrogen which could react with oxygen or recombine further down the tube at a considerable distance from the catalyst. While it is thermodynamically impossible for the palladium to act by shifting the $H_2 \rightleftarrows 2H$ equilibrium and thereby manufacture atomic hydrogen in excess of its exceedingly small equilibrium concentration, the mechanism

$$PdO + H_2 \longrightarrow PdOH + H\uparrow \text{ and } PdOH + H_2 \longrightarrow PdOH_2 + H\uparrow$$

is entirely orthodox and made exceedingly likely in this case where a film of oxygen is known to adhere firmly to a palladium surface.

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[10] Benton and White, THIS JOURNAL, 52, 2325 (1930).

[11] Langmuir, *Trans. Faraday Soc.*, *17*, 607 (1921); Taylor, THIS JOURNAL, 53, 578 (1931).

[12] Elgin and Benton, *ibid.*, 51, 7 (1929).

[13] Polyakov, *Naturwiss.*, 16, 131 (1928); see also Chem. *Abstracts*, 24, *4434* (1930).

Professor H. S. Taylor has pointed out to me an even more illuminating example: a paper where Mitchell and Marshall[14] demonstrated that hydrogen passed over a platinum catalyst yielded what was undoubtedly monatomic hydrogen only if the gas contained a small amount of oxygen. The hydrogen atoms could reduce copper oxide at 5.5 cm. distance from the catalyst.

Additional applications of this type of reaction, the oxidation of carbon disulfide, of carbon monoxide and of the hydrocarbons are discussed subsequently.

Once the reaction chains have been initiated, what is their course? Thompson and Hinshelwood's data can be best interpreted by assuming that the chains which are set up are both straight and branching, the latter predominating at higher pressures and temperatures. This may be due to a reaction slightly endothermic such as

$$\mathrm{H} + \mathrm{H_2} + \mathrm{O_2} \longrightarrow \mathrm{H} + \mathrm{OH} + \mathrm{OH} - 14\mathrm{K.\ cal.}$$

In an unpacked bulb the rate of reaction, therefore, increases very rapidly with temperature until the chains become so branching that explosion occurs.

Halving the pressure will cut down the reaction rate many-fold; this effect will be most pronounced at high temperatures, where branching predominates. This is confirmed in Gibson and Hinshelwood's results where the ratio of reaction rate, time for half change, at 600 mm. to the rate at 300 mm. of $2\mathrm{H_2} + \mathrm{O_2}$ gas mixture is 3.7 at 529° but 18.9 at 569°. In fact this result seems to indicate that there is little if any branching at 529°, so that one must distinguish between the branching-chain, high-temperature explosion at $>570°$, and the low-pressure explosion at 500°, which as pointed out subsequently may consist only of a very large number of straight chains.

In the packed bulb, chains are broken too soon to permit much branching. The reaction increases less slowly with temperature. Explosion is delayed until much higher temperatures, representing maximum branching. Halving the pressure hardly affects the reaction rate until very high temperatures are reached. Gibson and Hinshelwood found that in a packed vessel the rate at 600 mm. was the same as that at 300 mm. at 529°, and 1.8 faster at 569°.

The retarding effect of packing should be greater under those conditions favoring branching chains, *i. e.*, high temperature and pressure. Actually it becomes so great as to counterbalance the catalytic effect of walls initiating chains; the reaction is less in the packed vessel.

	Ratio of rate with porcelain to rate without	
Temp., °C.	*at 600 mm.*	*at 300 mm.*
529	4.1	15.6
569	0.3	8.1

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[14] Mitchell and Marshall. *J. Chem. Soc.*, 123, 2448 (1923).

Change of Adsorbed Gas **Layer** at the upper Explosion Pressure.—At the beginning of the paper we mentioned the curious abruptness with which the explosive reaction replaces the non-explosive, as one passes the upper explosion limit. Why does the latter, which is becoming slower and slower as the pressure is lowered, suddenly become explosive?

The answer is that there is a sudden change in the adsorbed gas layer responsible for the initiation of the reaction chains.

At this point we wish to draw an analogy with experiments by Langmuir.[15] Hydrogen and oxygen do not react on a tungsten filament at 1500°K. There is, instead, a unimolecular film of oxygen which shields the tungsten surface and prevents it from dissociating the hydrogen as it normally does in the absence of oxygen. The oxygen forces are directed inward toward the tungsten, WO_3 forms and distils off, and the oxygen is gradually consumed. At the point where less than a unimolecular film of oxygen remains, it can no longer ward off the hydrogen, the hydrogen gets in and "making a flank attack on the oxygen" rapidly reacts with it to form steam, and almost instantaneously sweeps the surface bare of oxygen. Thereafter, the normal dissociation of hydrogen into atoms on the tungsten surface sets in.

In our case, with a silica vessel, at 500° and pressures of several hundred millimeters, the gas layer is reversed and the walls are covered with hydrogen, to the exclusion of oxygen. When the pressure is lowered some of the hydrogen is desorbed. This, as well as the branching effects discussed above, slows down the non-explosive reaction. We know this from adsorption measurements such as those presented in Table V, and by analogy with desorption of hydrogen on nickel. However, there is still enough hydrogen to prevent the oxygen from entering the surface layer, just as the oxygen layer on tungsten warded off the hydrogen.

The upper explosion pressure limit is reached. Further reduction in pressure results in the hydrogen sheath losing its power to exclude oxygen from the surface. This may be caused either by a small desorption of hydrogen, or a large stepwise desorption similar to that found by Benton and White,[10] where a small reduction of hydrogen pressure resulted in the sudden desorption from nickel of a third of all the adsorbed hydrogen. In this way the hydrogen sheath is broken open to a flank attack by the oxygen, excess hydrogen swept from the surface and the surface exposed to equal bombardment by oxygen as well as hydrogen.

The original hydrogen-covered surface released hydrogen atoms into the gas phase at a slow rate such that the ensuing reaction was non-explosive. We cannot predict the new type of surface reaction which will be suddenly produced below the explosure pressure. The nature of the adsorbed gas has been radically altered, and there is no objection to assuming that it

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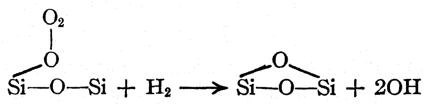
[15] Langmuir, THIS JOURNAL, **38,** 2271 (1916).

might initiate chains much faster than the hydrogen-covered surface, in fact so fast that explosion occurs. **A** possible reaction is



where the energy necessary to produce 2OH from $H_2 + O_2$ (only 14 cal.) is supplied by the formation of the Si–O bond. This cannot happen of course if the Si–O is covered with hydrogen, *i. e.*, Si–OH, at higher pressures.

The Lower Explosion Limit.—Professor Haber[2] has already suggested as the cause of the lower explosion limit, AB, Fig. 1, an insufficiency of triple collisions at low pressure to carry on the chain step $H + O_2 + H_2 \longrightarrow H_2O + OH$, which explains why, below the identical lower pressure limit, neither the thermal explosion[1,3] nor the spark explosion[16] occurs.

Explanation of Factors Influencing Explosion.—In addition to what has already been said explaining phenomena connected with the non-explosive reaction, such a mechanism satisfies explosive characteristics as well. The upper explosion limit is independent of packing in such similar surfaces as quartz, glass and silica, because it marks the pressure at which oxygen first gains admission to the surface, independent of the amount of surface present. Surfaces of iron and copper give the same qualitative results. Aluminum was expected to be ineffective in causing the explosion, and indeed such was found to be the case. Professor Taylor has called my attention to the similarity between an alumina surface and Langmuir's oxygen-coated tungsten filament.[15] In both instances the covering of oxygen atoms is so tightly bound, chemically, to the metal surface that activity in catalyzing the combination of hydrogen and oxygen is completely paralyzed. No explosion results,

Pretreatment with hydrogen saturates the walls and thereby delays explosion. Of course, the hydrogen may also prevent explosion by poisoning the surface with excess steam.

Excess of hydrogen naturally means one must exhaust to lower total pressures of oxy-hydrogen gas before the hydrogen sheath is broken. The significance of the last column in Table II now becomes apparent: it is the hydrogen pressure below which oxygen gains access to the silica surface.

Other Reactions.—There is every reason to expect that a great many other chain reactions may be initiated at the walls and extend into the gas phase by such a mechanism as we have proposed above. Moreover, in addition to the normal non-explosive reaction, there is always a possibility in each of these cases of sudden change in the nature of the adsorbed gas layer, and a corresponding sudden alteration in reaction velocity upon lowering the pressure. The explosion characteristics of the hydrogen–

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[16] Kowalsky, *Z. physik. Chem.*, [B] 11, 56 (1930).

oxygen reaction are probably to be met with in numerous reactions. Several such reactions in the field of oxidations are given.

Oxidation of Carbon Disulfide.—It has already been confirmed by H. W. Thompson[8,17] that this reaction simulates the hydrogen-oxygen reaction. Reaction chains are initiated at above 150° at a wall doubtless covered with carbon disulfide, which by a mechanism analogous to that postulated above for the generation of hydrogen atoms liberates oxygen atoms into the gas phase. These will react with carbon disulfide in the gas phase, as Kopsch and Harteck[18] have shown, and the reaction chain be propagated as usual. As the pressure is lowered explosion sets in at 200 mm. This would be interpreted to mean that the carbon disulfide is sufficiently desorbed from the glass surface at this point to permit oxygen to gain access to the surface layer, giving rise to a new explosive surface reaction. Carbon disulfide and oxygen flowing from two concentric tubes explode at a much lower temperature[19] (107°) than under the usual static[8] measurements (140°). This is to be expected because the surface of the oxygen tube should undoubtedly be relatively free from adsorbed carbon disulfide, and, therefore, favorable to initiate explosion at much lower than the normal temperatures.

Oxidation of Carbon Monoxide.—This proceeds at about 650°, presumably initiated on the walls by reaction with adsorbed carbon monoxide. Even at these high temperatures oxygen is still not appreciably adsorbed in an active state.' However, if the chains are initiated by the release of oxygen atoms into the gas phase, the oxidation reaction would proceed by subsequent interaction with water, and not by direct reaction with gaseous carbon monoxide.[20] As the pressure of the gases at 650° is lowered to 100 mm., the same phenomenon appears as in the hydrogen-oxygen reaction: due to the possible desorption of carbon monoxide the surface is suddenly bared to attack by oxygen and explosion results.[3]

Oxidation of Hydrocarbons.—Pease[21] has demonstrated that the oxidation rate of propane decreases several-fold as the temperature is raised from 300 to 425°, but that above this temperature it explodes. The presence of hydrogen has no effect at the lower temperatures, but above 425° it completely inhibits explosion. It is possible that at 300° the surface is covered with propane. As the temperature is raised, propane is desorbed, and the measurable reaction between oxygen and adsorbed propane decreases. At 425° the propane sheath becomes permeable to oxygen and with the new type of adsorbed gas layer explosion occurs.

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[17] Thompson, *Naturwiss.*, 18, 531 (1930).

[18] Kopsch and Harteck, *Z. Elektrochem.*, 36, 714 (1930).

[19] Dixon, *Rec. trav. chim.*, 44, 305 (1925).

[20] Jackson and Kistiakowsky, THIS JOURNAL, 52, 3471 (1930); Farkas, Goldiinger and Haber, *Naturwiss.*, 12, 266 (1930).

[21] Pease, THIS JOURNAL, 51, 1839 (1929).

The hydrogen inhibits only above 425° because below this temperature it is not appreciably adsorbed. Our measurements, Table V, Fig. 3, make it probable that above 425°, however, it would effectively poison the surface and prevent propane explosion.

Post-Explosion.—Farkas, Haber and Harteck[22] observed that if, within two minutes after an oxygen–hydrogen mixture has been exploded by a spark, a fresh supply of gas is admitted to the reaction vessel, explosion occurs even at 420, 20° lower than the lowest normal explosion temperature. It is possible that the spark explosion removes adsorbed hydrogen from the walls, leaving them accessible to oxygen and in a still highly activated state sufficient to catalyze the explosion of the newly admitted gas.

The author wishes to thank Professor H. S. Taylor for his sympathetic interest in, and criticisms of, this paper.

Summary

1. The adsorption of hydrogen on glass increases tremendously above 450°. It is, therefore, adsorbed in a highly activated form not possible at lower temperatures.

2. This gas layer initiates reaction chains which extend out into the gas phase in the combination of hydrogen and oxygen at 500°.

3. Analogously, other chain reactions may be initiated from a layer of gas adsorbed on glass or metallic surfaces, as in the oxidations of carbon disulfide, carbon monoxide and the hydrocarbons.

4. The reaction rate of a hydrogen–oxygen mixture diminishes as the pressure is lowered. Below a certain pressure, however, it explodes. It is shown that the non-explosive and the explosive reactions differ strikingly from each other. The former is extremely sensitive to increase of reaction surface; the latter, not. Pretreatment of the walls with hydrogen, excess hydrogen in the gas mixture, steam and inert gases all accelerate the non-explosive reaction but prevent explosion.

5. These characteristics can be attributed to the controlling influence of the adsorbed layer of hydrogen gas. Explosion occurs at that pressure below which the surface ceases to be completely protected by the hydrogen

6. Desorption of carbon disulfide or carbon monoxide may similarly account for the sudden explosion of these gases in oxygen below a critical pressure, or for phenomena in the oxidation of the hydrocarbons.

PRINCETON, NEW JERSEY

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[22] Farkas, Haber and Harteck, *Z. Electrochem.*, **36**, 711 (1930).

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

A STUDY OF THE ELECTROLYTIC DETERMINATION OF COPPER IN THE PRESENCE OF PLATINIC ION[1]

BY T. LEONARD KELLY AND JOSEPH J. MOLLOY

RECEIVED FEBRUARY 5, 1931 PUBLISHED APRIL 6, 1931

In the procedure for the electrolytic determination of copper, as outlined by Fales,[2] it is recommended that the cathode should not be weighed until the electrolysis is completed, after which the copper is dissolved off by means of 6 molar nitric acid and then the cathode itself is weighed, the difference in weight being that of deposited copper. Such a procedure is deemed necessary in view of the fact that during electrolysis the anode may dissolve to the extent of several tenths of a milligram with subsequent plating out on the cathode.[3] Strange as it may seem this is the only reference to this phenomenon that may be found. According to Popoff,[3] since the platinum is plated over the copper, both the platinum and copper deposited are removed by the nitric acid and consequently there is no need of Fales' precaution.

The object of the present investigation was to determine whether the deposited platinum remained on or was removed from the cathode upon dissolving the copper deposit.

Experimental Procedure

The copper sulfate used was Baker's C. P., which had been recrystallized several times. The electrolyte was made by dissolving this copper sulfate in distilled water and making up to the proper concentration by dilution. These solutions were standardized by electrolysis, using a rotating platinum wire anode and platinum gauze cathode as electrodes. A current of 1.5 amperes was used, this being increased to 2.0 amperes during the last ten minutes of the electrolysis. Electrolysis was carried out in a tall form 300-cc. beaker, covered with split watch glasses, which was placed within a wide-mouthed one-liter beaker.

Fifty cc. of standard copper sulfate is placed in the 300-cc. beaker and 2 cc. of 16 molar nitric acid and 2 cc. of 18 molar sulfuric acid are added and the whole diluted to 200 cc. The same current density was used as in the standardization. After electrolysis had proceeded for about thirty minutes and the cathode was well covered with deposited copper, 1 cc. of the electrolyte was pipetted off and 1 cc. of a standardized platinic chloride solution was added. In this way no fresh surface of the electrode was

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

Vales, "Inorganic Quantitative Analysis," Century Book Co., New York, 1925, p. 386.

[3] Although C. W. Easley, THIS JOURNAL, 32, 1123 (1910), has reported only a slight solvent effect of chlorine on a platinum anode, it is a well-known fact that fairly high concentrations of nitric and sulfuric acids do have an appreciable effect. This is reported by Popoff, *ibid.*, 51, 1304 (1929), and has also been experienced by us in this Laboratory.

exposed. In every instance it was observed that the platinum was plated over the copper, this being evident from the darkening of the cathode deposit.

The electrolysis was made to proceed until no positive test for copper was obtained with sodium diethyl dithiocarbamate. A discussion of the method employed in using the indicator and the effect of interfering elements will be found below. The time required for complete deposition varied with the concentration of the copper sulfate used, ranging from fifty minutes for a 64-mg. deposit to ninety minutes for a 315-mg. deposit.

When deposition was complete the cathode was removed in a manner which was partly the method of Beans and Stillman[4] and partly the siphon method as described by Popoff.[5] At the end of the electrolysis, distilled water was run into the electrolyte until the outside beaker was two-thirds full. Then the whole was gradually lowered, distilled water being played upon the cathode as the copper deposit was exposed, the current being shut off only when the electrodes were completely out of the electrolyte. The method resulted in practically no loss of cathode deposit, is efficient, requires but little time and obviates the use of a siphon.

After the cathode was removed it was washed with distilled water, then 95% alcohol, dried and weighed. The copper was now dissolved in 6 molar nitric acid, the cathode washed in distilled water, then in 95% alcohol, dried and weighed. Thus any increase in weight of the cathode over the original weight would be due to the platinum which had plated out on it and had not been dissolved off during the solution of the copper. *In every case the cathode gained in weight.*

The electrolyses were run using various concentrations of the copper sulfate solution and adding 1 cc. of platinic chloride solution, which was also varied in concentration. In this manner we studied the effect of the weight of the copper deposit and also the

TABLE I

EXPERIMENTAL RESULTS

Expt.	Initial wt. of cathode, g.	Cu added to soln., g.	Pt added to soln., g.	Wt. of cathode and deposit, g.	Final wt. of cathode. g.	Gain in wt., g.
1	14.7263	0.0637	0.004	14.7931	14.7280	0.0017
2	14.7275	.0637	.002	14.7930	14.7293	.0018
3	14.7292	.0637	.001	14.7939	14.7300	.0008
4	14.7300	.0637	.001	14.7946	14.7309	.0009
5	14.7307	.1274	.002	14.8598	14.7321	.0014
6	14.7321	.1274	.002	14.8610	14.7337	.0016
7	14.7337	.1274	.001	14.8622	14.7346	.0009
8	14.7367	.3130	.001	15.0506	14.7373	.0006
9	14.6653	.0637	.004	14.7322	14 6683	,0030
10	14.6682	.0637	.002	14.7335	14.6696	.0014
11	14.6694	.0637	.001	14.7341	14.6703	.0009
12	14.6703	.0637	.001	14.7348	14.6711	.0008
13	14.6710	.1274	.002	14 8000	14.6723	.0013
14	14.6722	.1274	.002	14.8014	14.6740	.0018
15	14.6738	.1274	.001	14.8020	14.6748	.0010
16	14 6758	.3130	.002	14.9904	14.6773	.0015
17	14 6773	.3130	.002	14.9918	14.6784	.0011
18	14.6783	.3130	.001	14.9923	14.6792	.0009
19	14.6792	3130	.001	14.9931	14.6801	.0009

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[4] J. W. Stillman, "New Direct Method for the Electrolytic Determination of Copper," Dissertation, Columbia University, 1920.

[5] Ref. 3, p. 1303.

effect of the concentration of platinum on the increase in weight of the cathode. These results are given in Table I.

In order to show that the amount of platinum remaining on the cathode seems to be a function of the amount of platinum present in the electrolyte and not on the amount of copper deposited, the following tables are arranged. Table II shows the result of the experiments with one milligram of platinum present and Table III shows the result of the experiments with two milligrams of platinum added to the electrolyte.

TABLE II

RESULTS OF EXPERIMENTS

Expt.	Cu added to solution, g.	Pt added to solution, g.	Pt remaining on cathode, g.
3	0.0637	0.001	0.0008
4	.0637	.001	.0009
7	.1274	.001	.0009
8	.3130	.001	.0006
11	.0637	.001	.0009
12	.0637	.001	.0008
15	.1274	.001	.0010
18	.3130	.001	.0009
19	.3130	.001	.0009
		Mean	0.00085

TABLE III

EXPERIMENTAL DATA

Expt.	Cu added to solution, g.	Pt added to solution, g.	Pt remaining on cathode, g.
2	0.0637	0.002	0.0018
5	.1274	.002	.0014
6	.1274	.002	.0016
10	.0637	.002	.0014
13	.1274	.002	.0013
14	.1274	.002	.0018
16	,3130	.002	.0015
17	,3130	.002	.0011
		Mean	0.0015

These results show that even though there would not be any platinum in the electrolyte at the beginning of a copper determination, the platinum which might dissolve off the anode will deposit not only over the copper but also ***through*** it, because the platinum was not added in our experiments until a heavy deposit of copper was deposited on the cathode. Also it will be seen that all of the platinum which is deposited on the cathode is not removed by the solution of the copper deposit by the nitric acid. Therefore the procedure outlined by Fales, *viz.,* deposit the copper, weigh, dissolve off the deposit and then weigh the cathode, will take care of any additional weight which might be due to solution of the anode and subsequent deposition on the cathode.

As stated above, the indicator used to determine when deposition was complete was sodium diethyl dithiocarbamate. This indicator was introduced by Callan and Henderson.[6] It is used as follows: 1 cc. of the electrolyte is pipetted into a 100-cc. Nessler cylinder, diluted with distilled water, made ammoniacal, 10 cc. of a 0.1% solution of the indicator added and the whole diluted to 100 cc. and well mixed. If copper is present, a clear brownish-yellow color is obtained. This is then matched against a standard, in a Duboscq colorimeter, the standard containing 0.00001 g. of copper per cc. It was found that a decided test for copper could be obtained with a solution containing 0.001 mg. with this indicator. Callan and Henderson have investigated the effects of iron, lead and zinc on the use of this indicator. Since these are not the only elements which are encountered in copper determinations, we thought it would be well to determine the effects of others which are found in these analyses. They are as follows.

NICKEL.—If present, even to the extent of one milligram per 100 cc., nickel gives a decidedly light green precipitate which interferes with the copper reaction. No method of overcoming this difficulty was found.

CADMIUM.—Cadmium gives a cloudy white turbidity which interferes with the copper reaction. No method of overcoming this difficulty was found.

ARSENIC.—As arsenate ion, even when present in fairly large quantities, arsenic does not interfere; as arsenite, however, unless the solution be made strongly ammoniacal, it will yield a white turbidity if present in excess of one milligram per 100 cc.

BISMUTH.—This element presented many difficulties, chief among them being the fact that even after the ammoniacal solution was filtered the filtrate showed a higher concentration of copper than was added. If the solution is made ammoniacal, boiled and filtered and then treated with the indicator, this difficulty is obviated.

Manganese, aluminum and magnesium, which are now encountered in the new light weight alloys, will not interfere with the copper reaction if the ammoniacal solution is boiled and filtered before adding the indicator.

Summary

1. From a study of the electrodeposition of copper in the presence of platinic ion, it has been found that the platinum deposits not only over the copper but also through it, causing an increase in weight of the cathode. It is therefore recommended that the cathode be weighed after the copper is dissolved off, instead of weighing before the deposition, in order to obtain the true weight of the cathode.

2. It has also been shown that the weight of the copper deposited,

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[6] Callan and Henderson, *Analyst.* 54, 650 **(1929).**

within limits, does not affect the amount of platinum remaining on the cathode after solution of the copper deposit.

3. The effects of certain elements on the use of diethyl dithiocarbamate as an indicator for copper have been shown.

WORCESTER, MASSACHUSETTS

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

SOLUTIONS OF SALTS IN PURE ACETIC ACID. IV. CUPRIC ACETATE AND AMMONIUM CUPRIC ACETATE

BY ARTHUR W. DAVIDSON AND ERNEST GRISWOLD

RECEIVED FEBRUARY 6, 1931 PUBLISHED APRIL 6, 1931

Introduction

In the first article of this series,[1] it was mentioned that cupric acetate is but slightly soluble in pure acetic acid, and that its solubility is markedly increased upon the addition of ammonium acetate; it was suggested that in this respect the cupric and ammonium acetates might be regarded as analogous to the corresponding hydroxides, whose interaction in aqueous solution is so familiar a phenomenon. No quantitative solubility data for cupric acetate in anhydrous acetic acid have been reported previously. Sandved,[2] however, determined the isotherm for the ternary system cupric acetate–acetic acid–water at 25°, and a short extrapolation from his data indicates the solubility in the pure acid to be about 0.24 mole per cent. of cupric acetate, the solid phase being the acid salt $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$. In the present investigation the solubility of cupric acetate over a range of temperatures has been measured, both in pure acetic acid and in the presence of ammonium acetate in varying concentration. The effect of potassium acetate, at one concentration, was determined also. Consideration of the results obtained has led to certain new ideas, which will be developed below, with respect to the analogy between these solvent effects and the corresponding phenomena in aqueous solution.

Method

Preparation of Materials.—The acetic acid, ammonium acetate and potassium acetate employed were all prepared as described in the second paper of this series.[3] The anhydrous cupric acetate used was prepared by recrystallizing the hydrate from solution in dilute acetic acid, and dehydrating at 90° until analysis showed no water to be present. Samples of the product, which was dark bluish-green, were analyzed for copper by the electrolytic and by the iodimetric method, and gave closely concordant results, averaging 34.99% of copper (calcd. for $Cu(C_2H_3O_2)_2$, 35.00%).

Binary System.—The solubility of cupric acetate in pure acetic acid was determined

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[1] Davidson, THIS JOURNAL, 50, 1890 (1928).

[2] Sandved, *J. Chem. Soc.*, 2967 (1927).

[3] Davidson and McAllister, THIS JOURNAL, 52, 507 (1930).

by the freezing point method previously described,' large stoppered test-tubes provided with thermometer and stirrer being used for the freezing point determinations. Short-range calibrated thermometers were employed, and each freezing point was determined at least twice. The equilibrium temperatures reported are believed to be correct to within 0.2".

Ternary System.—In the study of the solvent effect of ammonium acetate, the method described in the preceding paper of this series[4] was employed. Acetic acid solutions were prepared containing 7.9, 11.6, 15.1, 20.7, 22.1 and 23.7 mole per cent., respectively, of ammonium acetate. Known amounts of cupric acetate were dissolved in these solvents, and the equilibrium temperatures were determined just as in the binary systems. In these cases, however, due to the greater viscosity and deeper color of the solutions, the same degree of accuracy could not be attained; most of the temperatures reported, however, are believed to be correct to within 1°. By plotting these temperatures as ordinates against the mole percentages of cupric acetate as abscissas, a series of curves was obtained, each representing the variation with temperature of the solubility of cupric acetate in a solution having a fixed value of the ratio, number of moles of ammonium acetate/number of moles of (ammonium acetate + acetic acid), which ratio will hereafter be referred to as R.

Analysis of Solid Phases.—Samples of the solid phases present at equilibrium were obtained by crystallization from the solution under suitable conditions, followed by filtration and rapid drying between porous tiles. When the compound contained only cupric acetate and acetic acid, determination of copper by the electrolytic or iodimetric method sufficed to fix its composition. When a qualitative test showed ammonia to be present in the solid phase, however, a portion of the sample was analyzed for copper as above, and another portion for ammonia by addition of sodium hydroxide solution, followed by distillation into standard hydrochloric acid.

The data obtained are tabulated below, and are represented also in the accompanying diagrams. The concentration of cupric acetate in the solution is expressed throughout in mole percentage, and the equilibrium temperature is denoted by T.

Results

I. Binary System $Cu(C_2H_3O_2)_2$–$HC_2H_3O_2$.—The solutions were bluish-green, and showed no change in color on heating.

(a) Solid phase $HC_2H_3O_2$

$Cu(C_2H_3O_2)_2$, %	0.0	0.0307	0.0471	0.0831	0.0994
T	16.65	16.63	16.50	16.43	16.57

(b) Solid phase $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$

$Cu(C_2H_3O_2)_2$, %	0.169	0.236	0.266	0.305	0.408
T	25.3	30.1	32.4	35.0	41.5
$Cu(C_2H_3O_2)_2$, %	0.487	0.584	0.768	0.773	0.976
T	45.8	48.7	56.0	55.7	61.0

(c) Solid phase $Cu(C_2H_3O_2)_2$ (?)

$Cu(C_2H_3O_2)_2$, %	0.844	0.912	0.976
T	91.3	95.5	99.0

The curve for this system is given in Fig. 1. The solubility of cupric acetate in pure acetic acid at 25° is found to be 0.166 mole per cent., a figure

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[4] Davidson and McAllister, THIS JOURNAL, 52,519 (1930).

somewhat smaller than that obtained by extrapolation from the data of Sandved.[2]

The solid phase (b) was light blue-green in color, and was quite unstable, rapidly losing acetic acid vapor on exposure to the atmosphere. Because of this instability, a high degree of accuracy was not to be expected in its analysis; the percentage of $Cu(C_2H_3O_2)_2$ would tend to be too high. Five analyses for copper, in which the samples were handled as rapidly as possible before weighing, gave the following results (calculated to mole per cent. of $Cu(C_2H_3O_2)_2$): 51.14, 54.41, 56.02, 52.73, 50.28; average 52.93%. It is believed that these figures establish satisfactorily that the compound is the solvate $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$, previously reported by Sandved. In the neighborhood of 50° this compound undergoes transition to a dark bluish-green substance *(c)* which could not be obtained in sufficient quantity for analysis, but which appears to be unsolvated $Cu(C_2H_3O_2)_2$.

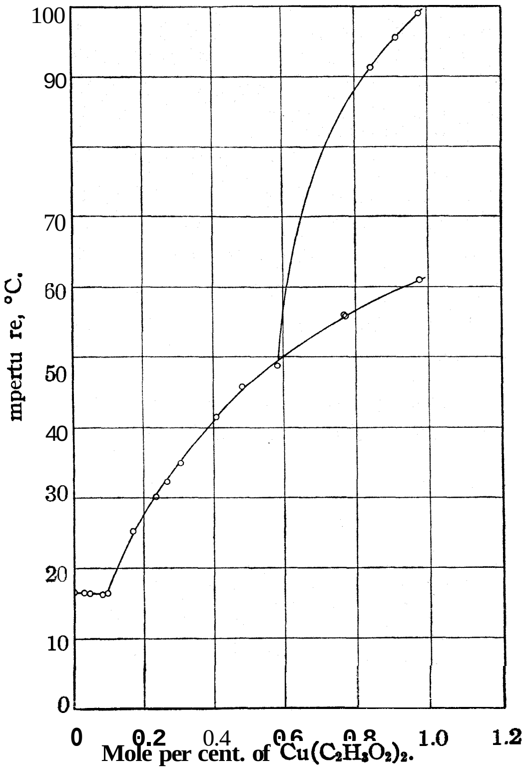

Fig. 1.—Solubility curve of $Cu(C_2H_3O_2)_2$ in pure $HC_2H_3O_2$.

II. Ternary System $NH_4C_2H_3O_2$–$Cu(C_2H_3O_2)_2$–$HC_2H_3O_2$.—These solutions were greenish-blue at ordinary temperatures. On heating, a marked deepening in color took place, together with a change toward the violet. At temperatures in the neighborhood of 120° for small values of R, or lower for the larger values, they attained a deep violet-blue color strongly reminiscent of aqueous cupric ammonia solutions; on cooling, they resumed their original greenish-blue color. This color change will be discussed later.

A. Mole ratio R = 0.079. Solid phase $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$

$Cu(C_2H_3O_2)_2$, %.	0.624	0.693	0.800	0.929
T	33.8	37.3	40.7	45.2

B. Mole ratio R = 0.116. Solid phase $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$

$Cu(C_2H_3O_2)_2$, %	0.816	1.026	1.179
T	32.5	38.5	42.7

C. Mole ratio R = 0.151. Solid phase $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$

$Cu(C_2H_3O_2)_2$, %	1.005	1.072	1.273	1.488	1.746
T	28.0	31.8	36.8	41.2	42.7

D. Mole ratio R = 0.207. (a) Solid phase $Cu(C_2H_3O_2)_2 \cdot 4NH_4C_2H_3O_2 \cdot 4HC_2H_3O_2$

$Cu(C_2H_3O_2)_2$, %	0.796	1.188	1.584
T	31.5	32.5	33.5

(b) Solid phase $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$

$Cu(C_2H_3O_2)_2$, %	1.708	1.766	1.890
T	37.0	40.7	41.8

E. Mole ratio R = 0.221. Solid phase $Cu(C_2H_3O_2)_2 \cdot 4NH_4C_2H_3O_2 \cdot 4HC_2H_3O_2$

$Cu(C_2H_3O_2)_2$ %	0.777	1.125	1.399
T	31.0	34.0	34.0

F. Mole ratio R = 0.237. Solid phase $Cu(C_2H_3O_2)_2 \cdot 4NH_4C_2H_3O_2 \cdot 4HC_2H_3O_2$

$Cu(C_2H_3O_2)_2$, %	0.448	0.532	0.765
T	48.C	50.5	64.0

The curves for this system are given in Fig. 2; for purposes of comparison, part of the curve for the binary system is reproduced here also. In series **A**, B, C and D (b), the solid phase was light blue-green in color, as in **(b)** of the binary system; qualitative tests showed it to contain no am-

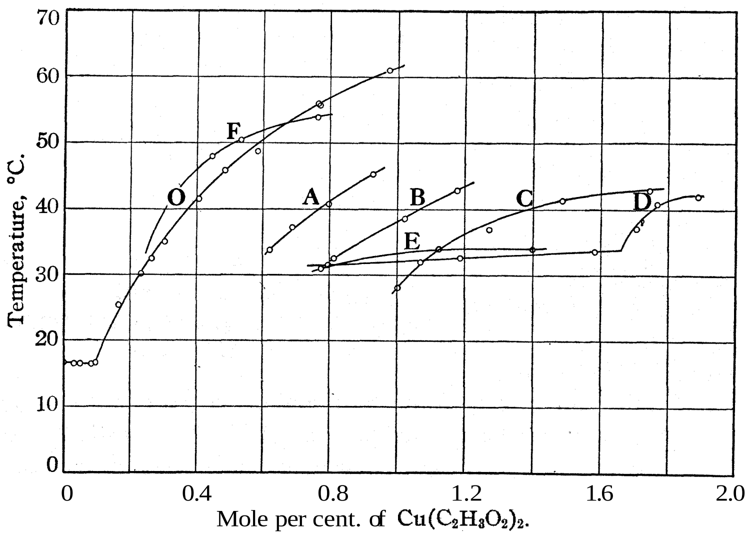

Fig. 2.—Solubility curves of $Cu(C_2H_3O_2)_2$ in $HC_2H_3O_2$ containing various concentrations of $NH_4C_2H_3O_2$: O, $R = 0$ (pure $HC_2H_3O_2$); A, R = 0.079; B, R = 0.116; C, R = 0.151; D, R = 0.207; E, R = 0.221; F, R = 0.237.

monia. No quantitative analysis of this compound was made, since its close resemblance in appearance and behavior to the solid phase which had been isolated, under similar conditions, from the binary system, was deemed sufficient to identify it as the same substance, namely, the solvated cupric acetate $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$. Further evidence of the correctness of this conclusion is to be found in the solubility isotherm of Fig. **3** (to be discussed in detail later); it will be seen that the solubility values for cupric acetate in pure acetic acid and at the lower concentrations of ammonium acetate fall upon a perfectly smooth curve, which could hardly be the case unless they referred to the same solid phase throughout this range.

In series D(a), E and F, the solid phase was quite evidently a different compound from that just discussed. It was deep blue in color, fairly stable on exposure to the atmosphere, and evolved ammonia on treatment with sodium hydroxide. In this case, the high viscosity of the mother liquor made its complete removal difficult; three quantitative analyses, however, gave the following results

	Mole, % $Cu(C_2H_3O_2)_2$	Mote, % $NH_4C_2H_3O_2$	Mole, % $HC_2H_3O_2$ (by difference)
	10.85	46.18	42.97
	9.49	43.49	47.02
	10.17	44.16	45.67
Average	10.17	44.61	45.22
Calcd. for $Cu(C_2H_3O_2)_2 \cdot 4NH_4C_2H_3O_2 \cdot 4HC_2H_3O_2$	11.11	44.44	44.44

These figures leave little room for doubt that the deep blue substance is a ternary compound, or solvated ammonium cupric acetate, of the composition given. No such compound has been reported previously, although an ammoniated cupric acetate of the formula $Cu(C_2H_3O_2)_2 \cdot 4NH_3$ is well known;[5] a hydrated ammonium cupric acetate, $2Cu(C_2H_3O_2)_2 \cdot NH_4C_2H_3O_2 \cdot H_2O$, is to be found in the literature,[6] and there is also some evidence for the existence of a hydrate of $Cu(C_2H_3O_2)_2 \cdot 4NH_4C_2H_3O_2$, although this compound has not been isolated in a pure state.[7]

It appears from these data that the solubility of cupric acetate in acetic acid at any fixed temperature between 30 and 45° increases with increasing concentration of ammonium acetate, so long as solvated cupric acetate is the stable solid phase. Upon the appearance of the ternary compound, however, the mole percentage of cupric acetate in the saturated solution begins to decrease with increasing ammonium acetate concentration. This is more clearly brought out in Fig. **3,** which represents an isotherm for 33.7°, plotted from data obtained from Fig. 2. It will be seen that the

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[5] Horn, *Am. Chem.* J., *39*, **184** (1908); see also Ephraim and Bolle, *Ber.*, 48, **638** (1915).

[6] Richards and Oenslager, *Am. Chem.* J., **17**, 297 (1895).

[7] Foerster, *Ber.*, **25**, 3416 (1892).

solubility of cupric acetate, which is 0.280 mole per cent. in pure acetic acid at this temperature, increases upon the addition of ammonium acetate until R is 0.207, when the solubility reaches a maximum of 1.66 mole per cent., and a new solid phase appears. Beyond this point the concentration of cupric acetate in the saturated solution diminishes very rapidly with further addition of ammonium acetate, falling to a value of no more than 0.25 mole per cent. (somewhat less than the solubility in acetic acid alone) at the highest concentration of ammonium acetate investigated (R = 0.237). Shortly beyond this point, when R = 0.258, the compound $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$ appears as solid phase.

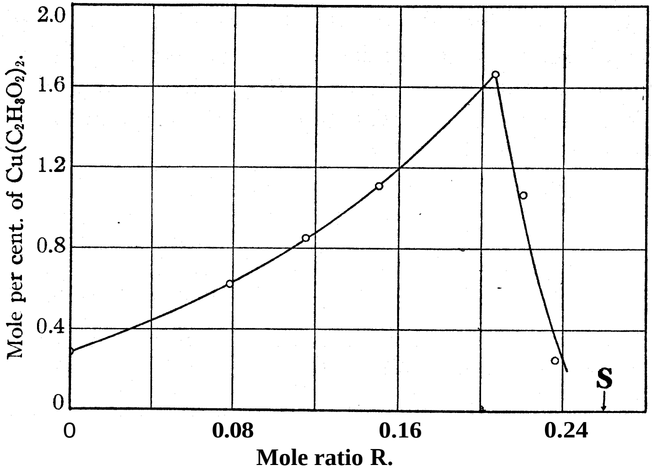

Fig. 3.—Effect of varying concentration of $NH_4C_2H_3O_2$ upon the solubility of $Cu(C_2H_3O_2)_2$ in $HC_2H_3O_2$ at a fixed temperature: isotherm at 33.7°. *S* indicates saturated solution of $NH_4C_2H_3O_2$.

In order to determine whether or not the solvent action upon cupric acetate, which has just been discussed, is due solely to the presence of ammonia, one further experiment was carried out, in which *potassium* acetate was employed as solvent. An acetic acid solution of the latter salt, in which R was 0.083, was found to dissolve 0.476 mole per cent. of cupric acetate at 33.7°. This is evidently of the same order as the solubility of the cupric salt in ammonium acetate solution under similar conditions One marked difference between the two cases, however, is worthy of mention. Although the potassium acetate-cupric acetate solution was very similar in color, at ordinary temperatures, to a corresponding solution containing the ammonium salt, yet in the former case no perceptible color change took place on heating; at 100° the colors of the two solutions were quite unlike. The possible significance of this fact will be considered in the following section.

Discussion

As was stated in the introduction to this article, when it was first discovered that cupric acetate readily dissolved in an acetic acid solution of ammonium acetate, we were disposed to regard this phenomenon as quite analogous to the solubility of cupric hydroxide in aqueous ammonium hydroxide. Superficially, indeed, besides the purely formal resemblance, there is a fairly close parallel between the observed facts in the two cases The solubility of cupric hydroxide increases with increasing concentration of ammonium hydroxide,[8] and although there is no satisfactory evidence as to the solid phase in equilibrium with concentrated solutions, the compound $Cu(OH)_2 \cdot 4NH_3$ is commonly supposed to be present in the solution.[8b,9] The ternary compound obtained in the present investigation might, correspondingly, be regarded as a solvated $Cu(C_2H_3O_2)_2 \cdot 4NH_3$. Further, as stated above, the violet-blue color which appears at high temperatures in the ternary solutions herein described, is strikingly similar to that of the aqueous solutions under discussion. But there are a number of considerations which tend to cast doubt upon the validity of this analogy. Foremost among these is the fact that solutions of ammonium acetate in acetic acid, unlike ammonium hydroxide in water, have no appreciable vapor pressure of ammonia at ordinary temperatures; the ammonium acetate is quite stable and gives every indication of being as strong a base as the corresponding potassium compound, which, indeed, it closely resembles. Not only are the freezing-point curves of potassium and of ammonium acetates in acetic acid very similar,[10] but it has been found that the two bases behave in exactly the same manner upon electrometric titration with strong acids.[11] It has just been shown, too, that the solvent action upon cupric acetate is not peculiar to the ammonium salt but is exhibited by potassium acetate to a similar degree. Furthermore, the isotherm obtained in this investigation is quite similar to that previously found[4] for the system sodium acetate–zinc acetate–acetic acid, and the ternary addition compounds obtained in the two cases are of the same nature, as may be seen by comparing the two formulas

$$Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$$
$$Cu(C_2H_3O_2)_2 \cdot 4NH_4C_2H_3O_2 \cdot 4HC_2H_3O_2$$

All of these facts point toward the conclusion that the solvent effect of ammonium acetate upon cupric acetate, at least at low temperatures, is due to the strongly basic nature of the ammonium compound, rather than to any specific effect of the ammonia which it contains, and that the analogous

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[8] (a) Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904); (b) Dawson, *Z. physik. Chem.*. **69**, 110 (1909).

[9] *De* Wijs, *Rec. tras. chim.*, **44**, 663 (1925).

[10] Ref. 3, p. 510.

[11] Hall, private communication.

phenomenon in aqueous solutions should be sought in the effect of strong alkalies, rather than of ammonium hydroxide, upon cupric hydroxide.

It is true that cupric hydroxide is not ordinarily regarded as amphoteric; but, as has frequently been pointed out,[12] the difference among the various metals in this respect must be regarded merely as one of degree. Cupric hydroxide is, indeed, appreciably soluble in concentrated aqueous solutions of sodium or potassium hydroxide, giving a deep blue solution, The most reliable quantitative data that have been obtained on this point appear to be those of Müller[13] for the system sodium hydroxide–cupric hydroxide–water. He found that the solubility of cupric hydroxide[14] in sodium hydroxide solutions at 18° increases, at first, with increasing concentration of alkali, reaching a maximum of about 0.3 mole per liter in approximately 12.5 molar sodium hydroxide solution. Here, however, a new solid phase appears, which is referred to as sodium cuprite, and is apparently of the formula $Na_2CuO_2{\cdot}2H_2O$, or $Cu(OH)_2{\cdot}2NaOH$, and from this point on the concentration of cupric hydroxide in the saturated solution decreases sharply with increasing concentration of alkali. The relationships in the ternary system studied in the present investigation are obviously quite similar to those just discussed, with the ternary addition compound, whose formula might alternatively be written $(NH_4)_4Cu(C_2H_3O_2)_6{\cdot}4HC_2H_3O_2$, playing the same part as the sodium cuprite in the aqueous system.[15] However, as in the case of the sodium zinc acetate discussed previously,[4] we are hardly prepared, as yet, definitely to characterize this compound; further study of its properties will be required before it can be determined whether or not it should be considered as a cuprite.[16]

In supposing the effect of ammonium acetate upon cupric acetate to be of the same nature as that of potassium acetate, and in drawing an analogy between these effects, on the one hand, and that of strong alkalies upon cupric hydroxide in aqueous solution, on the other, we have apparently disregarded the marked reversible deepening of color which occurs in the ammonium acetate–cupric acetate solutions, and in these alone, on heating. We suggest the following hypothesis[17] to account for this color change.

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[12] See, for instance, Goudriaan, *Rec. trav. chim.*, *39*, 505 (1920); Kraus, *Trans. Am. Electrochem. Soc.*, 45, 175 (1924); Franklin, THIS JOURNAL, 46, 2144 (1924).

[13] Müller, *Z. physik. Chem.*, *105*, 73 (1924).

[14] Cupric hydroxide was found to be metastable with respect to cupric oxide under these conditions; nevertheless its solubility could be determined.

[15] Just as the sodium cuprite is unstable in contact with pure water, and can exist only in the presence of concentrated sodium hydroxide solutions, so the ternary compound of this article is unstable in the presence of pure acetic acid.

[16] In the ammonia system, a compound of a somewhat analogous nature, having the formula $CuNK_2{\cdot}3NH_3$, or $CuNH_2{\cdot}2KNH_2{\cdot}NH_3$, was described by Franklin, THIS JOURNAL, 34, 1501 (1912), and was called by him potassium ammonocuprite. In this compound, however, the copper is in the cuprous, not the cupric, state.

[17] *Cf.* Ref. 1, p. 1894.

An ammonium acetate solution in acetic acid may, of course, be regarded, with equal validity, as a solution of *ammonia* in this solvent. At ordinary temperatures, as has been mentioned above, there is every reason to believe that the ammonia is completely combined with the solvent. As the temperature is raised, however, an increasing dissociation into ammonia and solvent doubtless occurs, just as in the case of aqueous ammonium hydroxide. It has, in fact, been shown[18] that the vapor pressure of ammonia from a concentrated solution of ammonium acetate in acetic acid at the boiling point must be appreciable, since the distillate from such a solution contains a perceptible quantity of ammonia. It therefore seems reasonable to suppose that while ammonium acetate in acetic acid at room temperature is comparable to potassium hydroxide rather than to ammonium hydroxide in aqueous solution, yet at temperatures above 100° it begins to exhibit properties analogous to those of aqueous ammonia at ordinary temperatures. The ammonia, then, being but loosely held by the solvent under these conditions, may be available for the formation of other ammonia complexes. If this hypothesis is correct, the violet-blue color which appears in the cupric acetate–ammonium acetate solutions at elevated temperatures may be due to a complexion, $Cu(NH_3)_n^{++}$, of the same nature as that which gives rise to a similar color in the aqueous cupric ammonia solutions.

Summary

1. The solubility of cupric acetate in pure acetic acid and in the presence of ammonium acetate in concentrations up to 23.7 mole per cent. has been determined at various temperatures.

2. The concentration of cupric acetate in the saturated solutions at a fixed temperature has been found to increase with increasing concentration of ammonium acetate as long as a solvated cupric acetate is the stable solid phase, but to decrease with further addition of ammonium acetate after the appearance of a ternary addition compound as solid phase.

3. A solvated ammonium cupric acetate of the formula $Cu(C_2H_3O_2)_2\cdot 4NH_4C_2H_3O_2\cdot 4HC_2H_3O_2$ has been isolated and analyzed.

4. The ternary system here studied has been compared with solutions of cupric hydroxide in concentrated aqueous alkali solutions, and certain resemblances have been pointed out.

5. An hypothesis has been advanced to account for the violet-blue color which appears at elevated temperatures in ammonium acetate–cupric acetateacetic acid solutions.

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[18] *Davidson, Trans. Kans. Acad. Sci.,* **31,** 60 *(1928).*

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

THE EFFECT OF AMMONIUM FORMATE UPON THE SOLUBILITY OF CUPRIC FORMATE IN FORMIC ACID

BY ARTHUR W. DAVIDSON AND VERNON HOLM

RECEIVED FEBRUARY 6, 1931 PUBLISHED APRIL 6, 1931

Introduction

In a previous article,[1] it was shown that the solubility of cupric acetate in anhydrous acetic acid is markedly increased in the presence of ammonium acetate, and comparisons were drawn between this phenomenon, on the one hand, and the analogous effects of alkalies and of ammonium hydroxide upon cupric hydroxide in aqueous solution, on the other. It seemed desirable to study the corresponding system in another solvent, in order to determine whether acetic acid were unique among non-aqueous media, in this respect, or whether the behavior referred to might be regarded as a more or less general effect of ammonia in systems of the type CuX_2–HX. For this investigation, formic acid was chosen as solvent; this substance is a liquid over a wide temperature range (8.5 to 100.5°), is readily prepared in a pure state, and is known to be a good solvent for numerous salts.

The solubility of cupric formate in anhydrous formic acid was found by Kendall and Adler[2] to be very small, the saturated solution at 140° containing less than 0.1 mole per cent. of solute; no further data are given. In the present work the solubility of cupric formate over a range of temperatures has been measured, both in pure formic acid and in the presence of ammonium formate in varying concentration. The effect of potassium formate, at one concentration, was determined also. The results were similar to, though not identical with, those obtained in acetic acid solution, as will be shown below.

Method

Preparation of Materials.—The formic acid employed was prepared from a good grade of 90% acid by dehydration with boric anhydride, B_2O_3, as suggested by Schlesinger and Martin.[3] The acid was allowed to remain for a week in contact with a slight excess over the theoretical quantity of boric anhydride; it was then distilled off, treated with a small amount of fresh dehydrating agent, and again allowed to stand for several days. Finally the liquid was decanted and distilled under reduced pressure. The product had a freezing point of 8.3 to 8.5°, and was practically 100% formic acid.

Ammonium formate was prepared by passing dry ammonia into 100% formic acid until complete solidification had occurred. The product was desiccated over 99% sulfuric acid, and was then found to have a melting point of 117–118°, agreeing with that reported by Kendall and Adler. Potassium formate was obtained by dissolving pure potassium carbonate in an excess of 90% formic acid, heating to expel carbon dioxide

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[1] Davidson and Griswold, THIS JOURNAL, 53, 1341 (1931).

[2] Kendall and Adler, *ibid.*, 43, 1470 (1921).

[3] Schlesinger and Martin, *ibid.*, 36, 1589 (1914).

evaporating off most of the excess acid, and then heating to 150° for several days and finally to 190° for about an hour. The product had a melting point of 168°, agreeing with that reported by Kendall and Adler.

In the preparation of pure anhydrous cupric formate, some difficulty was encountered. An aqueous solution of the salt was readily obtained by dissolving basic cupric carbonate in 50% formic acid and heating to expel carbon dioxide. On cooling to room temperature, crystals of the tetrahydrate separated out, The first attempt to dehydrate this compound by heating to constant weight at 80°, as recommended by Kendall and Adler, was entirely successful, yielding a bright blue product which showed, upon analysis by the electrolytic method, 41.35% of copper (calcd. for $Cu(CHO_2)_2$, 41.39%). Strangely enough, however, several attempts to obtain further quantities of the salt by this method failed, because the cupric formate was partially changed, on heating, to a dark brown substance of unknown chemical nature, before the dehydration was complete. A somewhat different procedure was therefore adopted. Instead of being allowed to cool to room temperature, the solution was maintained at 80°; the crystals separating out under these conditions consisted of the anhydrous salt[4] These crystals were pressed between porous tiles and then dried at 75° for ten hours. The resulting product showed no discoloration, and analysis proved it to be pure anhydrous cupric formate.

Binary System.—The solubility of cupric formate in formic acid was determined by the freezing point method previously described.[5] Large test-tubes, each fitted with a thermometer and a stirrer in such a manner as to exclude moisture, were used for the freezing point determinations. Four calibrated thermometers were employed, and each freezing point was determined at least twice. Because of the very low solubility, in this case, and the very minute amounts of solid phase which could be made to separate, the accurate determination of freezing points was a matter of some difficulty. However. the temperatures reported are believed to be correct to within 0.5°.

Ternary System.—In the study of the solvent effect of ammonium formate, the method described in previous articles[1,6] dealing with similar ternary systems was again employed. Preliminary experiments having shown that the solubility of the copper salt, at any given concentration of ammonium salt, was much smaller in this case than in the acetic acid system, rather high concentrations of ammonium formate were used. Formic acid solutions were prepared containing 1U.00, 19.73, 29.75, 33.54 and 43.75 mole per cent., respectively, of ammonium formate. Known amounts of cupric formate were dissolved in these solvents,[7] and the equilibrium temperatures were determined just as in the binary systems. Thus a series of curves was obtained, each of which represented the solubility of cupric formate, at various temperatures, in a solvent having a fixed value of the ratio, number of moles of ammonium formate/number of moles of (ammonium formate + formic acid); this ratio will subsequently be referred to as R.

Analysis of Solid Phases.—When the solid phase in equilibrium with the solution was obtainable in sufficient quantity to make it possible, samples were prepared for analysis by crystallization from the solution under appropriate conditions, filtration and drying between porous tiles as rapidly as possible, to minimize loss of formic acid. Qualitative tests showed no ammonia to be present in any of the solid phases. Cupric formate and formic acid being the only components, a quantitative determination of copper by the electrolytic method was sufficient to fix the composition of the compound.

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[4] Lossen and Voss, *Ann.*, ***266***, 33 (1891).

[5] See, for instance, Davidson and McAllister, THIS JOURNAL, ***52***, 507 (1930).

[6] Davidson and McAllister, ibid., ***52***, 519 (1930).

[7] The color of the solutions, at room temperature, was a blue resembling that of the cupric ion in aqueous solution; on heating, however, it changed to a deep violet-blue, This color change will be discussed later.

The data obtained are tabulated below, and are also presented graphically in the accompanying diagrams. The concentration of cupric formate in the solution is expressed throughout in mole percentage; T denotes the equilibrium temperature.

Results

I. Binary System $Cu(CHO_2)_2$–$HCHO_2$

$Cu(CHO_2)_2$, %	0.0045	0.0048	0.0066	0.0075
T	35	42	49	52

The curve for this system is given in Fig. 1. It is evident that the solubility of cupric formate at ordinary temperatures is extremely small, far below the maximum value of 0.1% that was given for 140° by Kendall and Adler. It was found impossible to determine equilibrium temperatures below 35°; however, the curvature was so slight as to make it possible to continue the curve to the eutectic point by extrapolation. The solubility at 25° is 0.0040 mole per cent., about one-fortieth of the value obtained for cupric acetate in acetic acid.' The solid phase appeared to be bright blue in color, but could not be obtained in sufficient quantity for analysis.

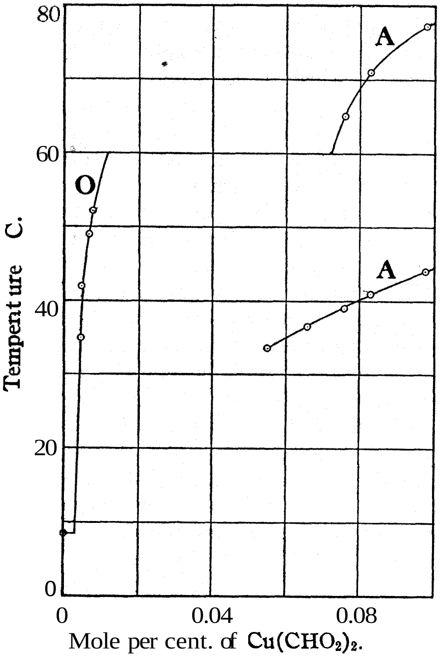

Fig. 1.—Solubility curves of $Cu(CHO_2)_2$ in pure $HCHO_2$ (Curve 0) and in 10% NH_4CHO_2 (Curve A).

II. Ternary System NH_4CHO_2–$Cu(CHO_2)_2$–$HCHO_2$

A. Mole Ratio R = 0.10

Two sets of equilibrium temperatures were obtained in this series, one corresponding to a stable, the other to a metastable equilibrium.

$Cu(CHO_2)_2$, %	0.055	0.066	0.076	0.083	0.098
T (unstable modification)	33.5	36.5	39	41	44
T (stable modification)	...	...	65	71	77

B. Mole ratio R = 0.1973

$Cu(CHO_2)_2$, %	0.319	0.399	0.465
T	60.0	70.5	77.2

C. Mole ratio R = 0.2975. Solid phase $2Cu(CHO_2)_2 \cdot 3HCHO_2$

$Cu(CHO_2)_2$, %	1.016	1.286	1.365
T	51.5	68.5	74.0

D. Mole ratio R = 0.3354. Solid phase $2Cu(CHO_2)_2 \cdot 3HCHO_2$

$Cu(CHO_2)_2$, %.	1,179	1.308	1.501	1 680	1.950	2.004
T....................	29.0	31.0	33.0	38.5	43.0	44.0

E. Mole ratio R = 0.4375. Solid phase $2Cu(CHO_2)_2 \cdot 3HCHO_2$

$Cu(CHO_2)_2$, % . . .	1.990	2.470	2 816	3 131
T.	37 0	43 5	48 5	51 5

The curves for this system are given in Fig. 2; the one for the lowest concentration of ammonium formate is shown also in Fig. 1, on the same scale as that used in the binary system, for purposes of comparison with the solubility curve of cupric formate in formic acid alone. In series A and B the solid phases were bright blue in color and similar in appearance to that obtained in the binary system; they contained no ammonia, and therefore consisted of cupric formate, presumably solvated. They could not be obtained in sufficient quantity for a reliable quantitative analysis, however.

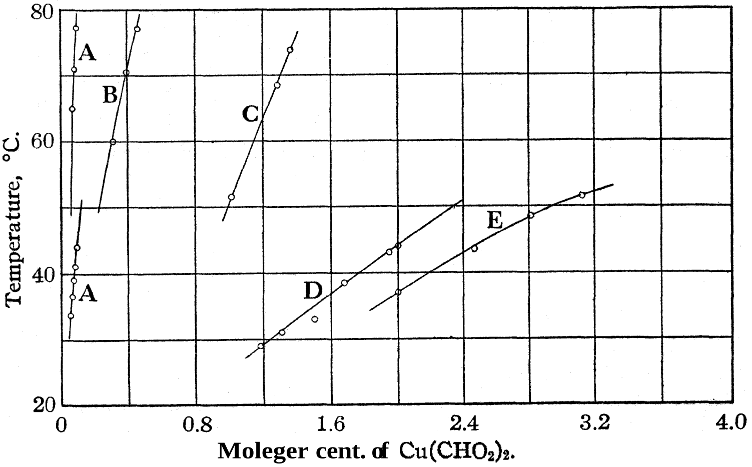

Fig. 2.—Solubility curves of $Cu(CHO_2)_2$ in $HCHO_2$ containing various concentrations of NH_4CHO_2: A, R = 0.10; B, R = 0.1973; C, R = 0.2975; D, R = 0.3354; E, R = 0.4375.

In series C, D and E, the solids isolated were pale blue in color. Qualitative analysis showed them to contain cupric formate and formic acid, but no ammonia. No acid cupric formate has been reported previously. Quantitative analysis gave the following results.

Series	% Cu	Mole % $Cu(CHO_2)_2$
C	28.65	40.26
D	27.78	37.96
E	28.11	38.82
Average	28.18	39.00
Calcd. for $2Cu(CHO_2)_2 \cdot 3HCHO_2$	28.56	40.00

It was impossible to attain a very high degree of accuracy in the analyses of these solid phases, because of the very small amounts of crystals obtainable, the difficulty in freeing them from the rather viscous adhering mother liquor, and their tendency to lose formic acid in vapor form on exposure to the atmosphere. However, it is believed that the figures given satisfactorily establish that the three substances analyzed are identical and that they consist of a solvated cupric formate, probably of the formula $2Cu(CHO_2)_2 \cdot 3HCHO_2$.

It is evident that the solubility of cupric formate in formic acid at a fixed temperature increases with increasing concentration of ammonium formate throughout the concentration range investigated, though not at a uniform rate. This is brought out more clearly in Fig. 3, which is an isotherm for 50°, plotted from the data of Fig. 2. At this temperature the solubility of cupric formate first increases as an almost linear function of R—the solid phase in this range being the bright blue compound of unknown degree of solvation—from 0.0068 mole per cent. in pure formic acid (R = 0) to 0.33 mole per cent. when R is 0.294. There a new solid phase—the pale blue solvate $2Cu(CHO_2)_2 \cdot 3HCHO_2$—appears, and the solubility then increases much more rapidly with increasing R, reaching a value of 2.95 mole per cent. at the highest concentration of ammonium formate investigated (R = 0.4375). A little beyond this point, at R = 0.51, NH_4CHO_2 appears as solid phase.

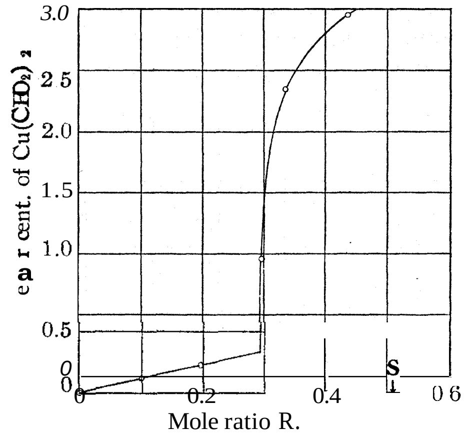

Fig. 3.—Effect of varying concentration of NH_4CHO_2 upon the solubility of $Cu(CHO_2)_2$ in $HCHO_2$ at a fixed temperature: isotherm at 50°. S indicates saturated solution of NH_4CHO_2.

In order to compare the solvent effect of potassium formate with that of ammonium formate, one further experiment, in which the former salt was used, was carried out. A solution in which R was 0.244 was found to dissolve 0.38 mole per cent. of cupric formate below 60°. This, as may be seen from the isotherm, is of the same order as the solubility of the cupric salt in ammonium formate solution under similar conditions.

Discussion

Comparison of Results with Data for the Corresponding Acetic Acid System.—It was shown in the previous article[1] referred to at the beginning of this paper that the solubility of cupric acetate in acetic acid at any fixed temperature between 30 and 45° is at first increased by the addition of ammonium acetate, a solvated cupric acetate being the stable solid phase in contact with these solutions. The data obtained in the present investigation show that this behavior is paralleled in the corresponding ternary system in formic acid, although the solubility of the cupric salt at any given value of R is much smaller in the latter case than in the former.

In the acetic acid system, at higher concentrations of ammonium salt, a ternary compound of the formula $Cu(C_2H_3O_2)_2 \cdot 4NH_4C_2H_3O_2 \cdot 4HC_2H_3O_2$ appears as stable solid phase, and the concentration of cupric acetate in the saturated solution then diminishes with increasing concentration of ammonium acetate. We expected to come upon a similar ternary compound in the formic acid system, but no such substance appeared, and the solubility of cupric formate continued to increase with increasing ammonium formate concentration throughout the range studied. It is, indeed, possible that a ternary compound might have been obtained as solid phase at still higher concentrations of ammonium formate, but this region could not be satisfactorily investigated.[8] It may be of interest to mention here that although no addition compound of cupric formate and ammonium formate appears to be known as yet, a compound of cupric formate and ammonia, having the formula $Cu(CHO_2)_2 \cdot 4NH_3$, has been reported.[9] We confirmed the existence of this compound by passing ammonia over a weighed quantity of cupric formate at 0° until no further increase in weight occurred; the amount of ammonia taken up closely corresponded to the above formula, and the product was blue-violet in color.

One further point of similarity between the two systems remains to be mentioned It was pointed out as a conspicuous property of the cupric acetate–ammonium acetate–acetic acid system that, on heating the solutions, a marked deepening of the blue color, accompanied by a change toward the violet, takes place. An exactly similar change was observed in the present investigation; at temperatures in the neighborhood of 100° for small values of R, or lower for the larger values, the ternary solutions attain a deep violet-blue color closely resembling that of aqueous cupric ammonia solutions; on cooling, they return to their original blue color. On the other hand, although solutions similar in color, at room tempera-

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[8] An attempt was made to employ as solvent a solution in which R was 0.50—an equimolecular mixture, that is, of ammonium formate and formic acid; but several circumstances made it impossible to obtain satisfactory results in this solvent. In the first place, since such a solution was supersaturated with respect to NH_4CHO_2 at temperatures up to 47°, the latter substance, rather than the copper compound, was likely to separate on cooling. Second, the very high viscosity of the solution promoted supercooling, as well as delayed the escape of air bubbles, and finally, the very deep blue color of the solution united with these other factors to make accurate observation of melting points a practical impossibility.

[9] Ephraim and Bolle, *Ber.*, 48, 1770 (1916).

ture, to those just discussed are readily obtained by the solvent action of potassium acetate and potassium formate upon the corresponding cupric salts in acetic acid and in formic acid, respectively, yet in these cases no color change whatever is observable on heating. The appearance of the violet-blue color in such solutions, therefore, is a phenomenon apparently occurring only in the presence of ammonium salts, is independent of the anion and may be due to the formation of some sort of cupric ammonia complex, as suggested previously.

Conclusions.—It was pointed out by Davidson and Griswold[1] that the water analog of the solubility of cupric acetate in acetic acid solutions of ammonium acetate at low temperatures is to be found in the solvent effect of the strong alkalies, rather than in that of ammonium hydroxide, upon cupric hydroxide, and it was suggested that only at temperatures above 100°, where the bond between the ammonia and the acetic acid may be supposed to be weakened, do the conditions approach those prevailing in an aqueous ammonium hydroxide solution at ordinary temperatures. The facts presented in this article are in complete accord with a similar hypothesis for formic acid solutions. Ammonium formate may obviously be regarded as a base in formic acid; here, it is true, there are no electrometric titration data available for comparing its basic strength with that of the corresponding potassium compound,[10] but the conductivity measurements of Schlesinger and co-workers[3,11] indicate that ammonium formate is highly dissociated, and give evidence of its being at least as strong a base as potassium formate, in this solvent. It is not surprising, therefore, that the solvent effects of the two bases upon cupric formate should be so nearly alike. However, the avidity of cupric formate for ammonia, on the one hand, and the characteristic violet-blue color, suggesting a cupric ammonia complex, that appears in hot cupric formate–ammonium formate solutions, on the other, make it seem probable that at high temperatures the free ammonia formed by dissociation also plays a part in the solvent action of ammonium formate.

Summary

1. The solubility of cupric formate in pure formic acid and in the presence of ammonium formate in concentrations up to 43.75 mole per cent. has been determined at various temperatures.

2. The solubility of cuprie formate at a fixed temperature has been found to increase, throughout this range, with increasing concentration of ammonium formate.

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[10] Very recently, a study of the potentiometric titration of acids and bases in formic acid solution has been published by Hammett and Dietz, THIS JOURNAL, 52, 4795 (1930). Ammonium formate was not investigated; urea, however, was found to behave as a strong base.

[11] Schlesinger and Calvert, THIS JOURNAL, 33, 1924 (1911).

3. A solvated cupric formate of the formula $2Cu(CHO_2)_2 \cdot 3HCHO_2$ has been isolated and analyzed.

4. The results here obtained have been compared with those previously reported for the corresponding ternary system in acetic acid. Attention has been called to the similarity between these two cases, and certain relationships with analogous aqueous systems have been pointed out.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE TRANSFERENCE NUMBERS OF POTASSIUM CHLORIDE. NEW DETERMINATIONS BY THE HITTORF METHOD AND A COMPARISON WITH RESULTS OBTAINED BY THE MOVING BOUNDARY METHOD

BY DUNCAN A. MACINNES AND MALCOLM DOLE[1]

RECEIVED FEBRUARY 10, 1931 PUBLISHED APRIL 6, 1931

We have obtained, in this Laboratory, by the moving boundary method a large amount of data, for the most part still unpublished, on the transference numbers of electrolytes. Many of these data differ so widely from the published values for transference numbers obtained by the Hittorf method that the question arose seriously in our minds as to whether the two methods (the Hittorf and moving boundary) obtain measures of the same property of the solutions of electrolytes. With potassium chloride, for instance, the measurements in dilute solutions by Jahn and associates[2] of the cation transference number by the Hittorf method gave values on the average 1% above the determinations by the moving boundary method. On the other hand, Dewey,[3] working at 0.2 N, obtained lower values for this constant by the Hittorf method than those obtained by MacInnes and Brighton[4] and Smith and MacInnes[5] using the moving boundary procedure. We have, however, found it possible to interpret the conductance and transference data, as a whole, for a group of simple electrolytes provided the newer moving boundary results are used. This is far from being true with reference to most of the Hittorf data now published. These new data and their interpretation will be the subject of a series of papers from this Laboratory. It was evidently very important to find out whether the disagreement of the results of the two methods for obtaining transference numbers is due to

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[1] Department of Chemistry, Northwestern University, Evanston, Illinois.

[2] Jahn and Bogdan, Z. *physik. Chem.*, 37, 673 (1901); Jahn and Hertz, *ibid.*, 58, 641 (1907). The "best values" of the "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, p. 310, are largely based on this work.

[3] Jane Dewey, THIS JOURNAL, 47, 1927 (1925).

[4] MacInnes and Brighton, *ibid.*, 47, 994 (1925).

[5] Smith and MacInnes, *ibid.*, 47, 1009 (1925).

experimental error or to a fundamental difference in the quantities measured. Hittorf and moving boundary measurements on solutions of potassium chloride were accordingly carried out, using all possible efforts to attain accuracy in the results. This paper will deal with the experimental details of the Hittorf measurements and their comparison with results obtained by the moving boundary method. The details concerning the latter will appear in another paper from this Laboratory.

The Hittorf Apparatus

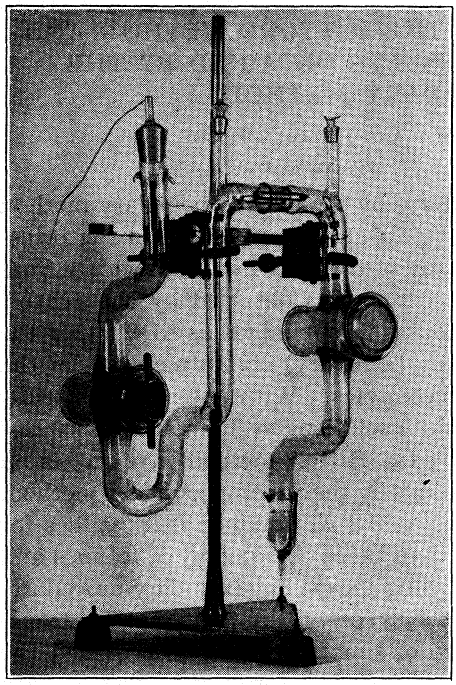

Fig. 1.

The apparatus, shown in Fig. 1, used for the Hittorf measurements was similar to that developed by Washburn[6] but differed from it in several details. It was made of Pyrex glass. A sufficient idea of the dimensions of the apparatus can be obtained from the data that the bore of the tubing used was 2 cm. and the full length of the tubing was 135 cm. The right angled turns of the tubes as shown were included for the purpose of breaking up convection currents due to heating, and were probably effective for the purpose because as soon as they were inserted in the apparatus the results showed a decided improvement. Convection currents were also minimized by the use of small current densities. A source of unequal heating along the tube which can cause convection is the bore of the large stopcocks. Though these were made the same size as the rest of the tube, adequate circulation of the thermostat water around them is not readily obtained. More adequate stirring around the portion of the solution in the bore of the stopcock was obtained by the design of stopcock shown in Fig. 1, and diagrammatically in section in Fig. 2. The usual key or handle for turning the stopcock has been cut away, leaving a hollow shell through which the thermostat water can flow freely. When it is necessary to turn the stopcock a metal key is inserted as is shown on the left-hand side of Fig. 1 and by dotted lines in Fig. 2. As an additional precaution against mixing, the thermostat (a 30 × 30 × 40 cm. glass battery jar) was mounted on the vibration-free support, which has been described in a previous paper.[7] The use of this support was also accompanied by an improvement in the results. The thermostat was stirred by a mechanism mounted independently of the vibration-free support. The stirring rate was regulated to produce no perceptible vibration of the thermostat.

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[6] E. W. Washburn, THIS JOURNAL, 31, 322 (1909).

[7] MacInnes, Cowperthwaite and Huang, *ibid.*, 49, 1710 (1927).

Preparation of Electrodes and Apparatus.—The anode was made from No. 23 B and S gage silver wire coiled into concentric helices to a diameter such that it would fit readily into the apparatus. It was carefully washed by standing it for several hours in distilled water. It was then dried in an oven, after which it was sealed into the glass stopper of the apparatus with de Khotinsky cement. If the silver appeared dark it was heated in a flame, or in an electric furnace to 400°, until the oxide or sulfide was decomposed. If this was not done there was a tendency for the solution in contact with the electrode to become alkaline. Since, during an experiment, the wire becomes coated with silver chloride, it was reduced electrochemically before the next determination. Twenty-five grams of the wire was necessary for the more concentrated solutions, and proportionately smaller amounts for the dilute solutions.

The cathode was also made of No. *23* silver wire coated electrolytically with silver chloride. It was cleaned thoroughly, usually by standing in distilled water overnight. It is very important that a thorough cleaning be carried out as the solution surrounding the electrode in the apparatus may readily become contaminated from occluded electrolyte. The cathode was dried for about an hour at 140°, after which it was sealed into the apparatus with cement.

Between each run the Hittorf apparatus was cleaned by allowing chromic acid to stand in it for some time. After rinsing with distilled water the apparatus was dried by playing a Bunsen flame over the surface while a current of dry air was passed through it. When dried the stoppers carrying the electrodes (previously greased and weighed) were inserted. The stopcocks, after being partly warmed, were greased with a commercial preparation.

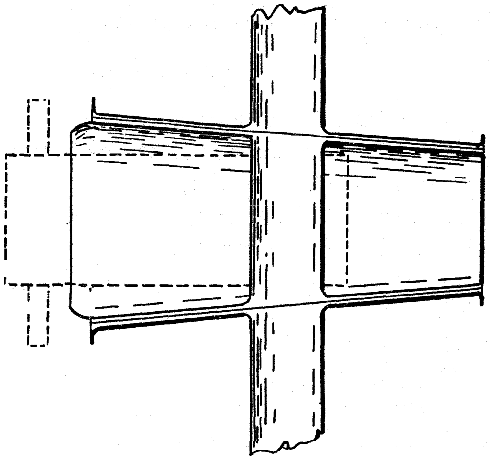

Fig.. 2.

Preparation of Solutions.—The solutions were prepared by weighing out the requisite amounts of potassium chloride and water to yield solutions of the desired normalities in equivalents per liter at 25°. The computation was made using the density data on potassium chloride solutions given in the "Critical Tables." An excellent grade of conductivity water was used in making up solutions. The potassium chloride was a C. P. grade which was further purified by precipitation with hydrogen chloride gas, followed by crystallization from conductivity water and proved to be free from sodium by spectroscopic test.

A difficulty encountered early in this research was that the cathode portion tended to become alkaline even though there was no trace of gas evolution at the electrodes. An investigation disclosed the fact that this alkalinity was due to dissolved oxygen which, presumably, entered into the reaction:

$$O + H_2O + 2e^- = 2OH^-$$

By saturating the solution with purified nitrogen there was no further tendency for the solution to become alkaline. All the work recorded in this paper was carried out using oxygen-free solutions. The proeedure for filling the transference apparatus with such solutions was as follows. The solution was placed in a special Erlenmeyer flask of a design already described.[8] A stream of purified nitrogen was first passed through a saturator containing the same solution as that in the special flask which followed it. The gas bubbled through the solution in that flask and then passed to the transference apparatus, which was furnished with an exit trap to prevent entrance of air. After running the gas for about one hour, which was sufficient to sweep out the oxygen from the solution and apparatus, a half turn of the head of the special flask caused the gas pressure to force the solution into the transference apparatus.

The Coulometers.—Two Richards type porous-cup coulometers were used, one at the anode end and another at the cathode end of the apparatus. Agreement of the weights of these two coulometers is evidence that no current has leaked away in the thermostat. The electrolyte was 10% silver nitrate solution, and No. 8 silver wire was used as anode. Platinum dishes of 75-cc. capacity were used for the more concentrated solutions, and platinum crucibles were used as cathodes for the more dilute solutions. The coulometers were covered with glass bell jars to protect them from dust particles.

The Electrolysis and Analysis

After the Hittorf apparatus was filled as described above, it was placed in the thermostat for at least one-half hour before the current was turned on, after which the electrolysis could be allowed to proceed overnight without attention. The current was supplied from small storage cells yielding about 15 volts. For the 0.02 *N* solution a current of 0.002 ampere was used. This was increased progressively for measurements with higher concentrations until a current of 0.045 ampere for the 3 N solutions was reached.

Following the electrolysis the solution in the apparatus was separated, according to Washburn's scheme, into anode, anode middle, middle, cathode middle and cathode portions. The anode and cathode portions were separated merely by turning the stopcocks. The other samples were drawn from the volume between the two stopcocks. The three middle portions were removed by suction directly into weight burets through clean dry glass tubing. The solutions in the two electrode portions were not removed into weight burets until the two portions into which the apparatus may be separated had been cleaned on the outside, weighed and the solution thoroughly shaken after opening the stopcocks. Portions of the resulting solutions were then transferred into weight burets. Each half of the apparatus, with its electrode, was dried and weighed, and the weight of the solution in each electrode portion could then be computed.

The analyses were carried out using the differential potentiometric method described by MacInnes and Dole.[8] Since the details of the method as applied to the determination of chlorides are given in that paper they will not be repeated here. However, a precision of about 0.003% is obtained in the analyses. With practice the determinations can be carried out quite rapidly, as many as six being possible in one day. The method has the great advantage of requiring no filtering or transfer of solutions, and

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[8] MacInnes and Dole, THIS JOURNAL, 51, 1119 (1929).

thus corrections for turbidity, etc., necessary with other precision methods for chlorides, are avoided.

Since the most concentrated solutions became turbid on dilution, it was evident that in such cases silver chloride from the electrodes was dissolving in the electrolyte. By allowing the diluted solution to stand, the colloidal material collected and could be filtered off and weighed and an appropriate correction made to the weight of the electrode portions.

The Results

A series of determinations at 0.1 N was made the results of which will not be tabulated, as they did not reach the accuracy of the later work. However, they demonstrated the desirability of the vibration-free support, the bends in the tubing of the Hittorf apparatus, and the air-free solutions, as well as minor experimental improvements. The data concerning the experimental results which attained the desired accuracy are given in Table I. This table is self-explanatory. Two figures for *a* weight or analysis refer to duplicate determinations. These agreements and the agreements of the analyses of the three middle portions give evidence of the accuracy of the work and of the, very essential, lack of mixing of the electrode and middle portions.

TABLE I

DATA CONCERNING DETERMINATIONS OF TRANSFERENCE NUMBERS OF POTASSIUM CHLORIDE AT 25°

Concentration	0.02 *N*	0.05 *N*	0.1 *N*	0.5 *N*	0.5 *N*	1.0 *N*	1.0 *N*	3.0 *N*	3.0 *N*
Amperes	0.002	0.0035	0.006	0.026	0.018	0.03	0.03	0.036	0.044
Volts	15	15	15	15	10	8	8	6	5
Time of electrolysis, hours	23	22	23	20.5	26	19.5	20.5	20.5	16.5
Wt. Ag in coulometers	0.16024 ,16043	0.3217 .3215	0.6136 .6135	2.1132 2.1128	1.9769 1.9767	1.9184 1.9180	2.4837 2.4833	2.8758 2.8756	2.7760 2.7756
Wt. anode portion	117.79	116.18	117.51	119.69	119.48	124.00	121.41	130.29	131.10
Wt. cathode portion	120.99	120.34	120.17	....	122.93	....	125.66	....	136.30
% KC1 in anode portion	0.10336 .10342	0.27963 ,27950	0.56662 .56665	3.0778 3.0780	3.1151 3.1151	6.6655 6.6660	6.5099 6.5100	19.1821 19.1814	19.207 19.203
% KCl in anode middle portion	.14932 ,14932	.37299	,74200 .74219	3.6520	3.6531	7.1502	7.1478	19.775	19.777
% KC1 in middle portion	,14948	.37297	....	3.6537 3.6539	3.6537	7.1474	7.1474	'19.776	....
% KC1 in cathode middle portion	.14939	,37302	,74206 ,74217	....	3.6543	7.1495	7.1485	19.777	19.775
% KCl in cathode portion	.19410 ,19398	,46274 ,46294	.91350 ,91369	....	4.1788 4.1784	....	7.7673 7.7668	....	20.329 20.327
KCl transferred anode	.05428	.1090	.20768	0.71470	0.6680	0.6457	0.8343	0.9655	0.9331
KCl transferred cathode	,05408	.1086	,20763	....	.6698	....	.8380	....	.9309
Trans. No. T_K (anode)	.4902	.4904	.4898	.4895	.4890	.4871	.4861	.4859	.4864
Trans. No. T_K (cathode)	,4884	,4884	,4897	....	.4903	....	.4882	....	.4853
Mean value T_K	.4893	,4894	.4898	.4895	.4896	.4871	.4871	.4859	.4858

Discussion of the Results

The average values of the cation transference numbers at each concentration are given in Table II, and, for comparison, the values by the moving boundary method obtained in this Laboratory by Dr. L. G. Longsworth, to whom we are indebted for permission to quote his results before their formal publication. It will be seen that, at the concentration at which measurements were made by both methods, there is quite extraordinary agreement

TABLE II

CATION. TRANSFERENCE NUMBERS, T_K, OF POTASSIUM CHLORIDE DETERMINED BY THE HITTORF AND MOVING BOUNDARY METHODS

Concn., N....	0.01	0 02	0.05	0.10	0.20	0.50	1.0	3.0
T_K, Hittorf...	....	.4893	.4894	.4898	...	.4896	0 4875	0.4857
T_K, M. B.....	0.4898	4896	.4900	.4899	.4891	..	....	....

Comparisons could not be made at higher concentrations because it is not yet possible to get accurate data by the moving boundary method at concentrations above about 0.2 *N*. That method is, however, accurate at concentrations so low that the chemical analyses necessary in the Hittorf method become difficult. It is interesting and most gratifying, that the two methods based on phenomena, superficially at least, so dissimilar should yield results that are in such excellent agreement.

As has been said in the introductory paragraph of this paper, these results differ quite widely from the measurements of previous workers in this field. That these early determinations led to values that differed considerably among themselves, and varied widely from later measurements is shown in Fig. 3.[9] Here the determinations, made between 18 and 30°, of the cation transference number of potassium chloride are given as ordinates against the cube root of the corresponding concentrations, the latter function being used only to obtain a convenient plot. Comparisons may be made of data in this temperature range because, within the experimental error, there is no apparent temperature coefficient of the transference number.[10] Washburn's solutions contained 0.1 mol of raffinose in addition to 1.24 mols of potassium chloride. The earlier moving boundary results will be considered in another paper.

It is not possible to assign, with certainty, reasons for the deviations of the earlier work from what we believe to be the correct values, particularly as there are many chances for obtaining inaccurate results with the Hittorf

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[9] Where determinations by the German workers yielded checks to 0.001 the points have been shifted slightly along the ordinates so as not to overlap. They can still, however, be read from the plot to the accuracy given.

[10] References to values plotted in Fig. 3 and not mentioned elsewhere in this paper are, Richter, *Z. physik. Chem.*, 80, 449 (1912), and Steele and Denison, *J. Chem. Soc.*, **81**, 456 11902).

method. Errors may arise from inaccurate analytical procedures, evaporation of the solvent, mixing of electrode and middle portions, electrical leaks, etc. An important source of error which would, since anion concentrations were determined, tend to give high cation transference numbers, particularly in the dilute solutions, is the fact that in the early work no correction was made for the conductance of the water used. It is difficult to estimate the magnitude of errors arising from this source. Ordinary distilled water would produce deviations of about 0.5% in the most dilute solutions. If the water stood for any time in soft glass containers, it could readily produce errors of several times this magnitude in the direction observed in Jahn's work. In the work described in this paper the best conductivity water was used. It was stored and measurements were made in Pyrex apparatus. No solvent correction was necessary within the experimental error in our Hittorf work. Small corrections have been made, for this effect, to the moving boundary data at the lower concentrations.

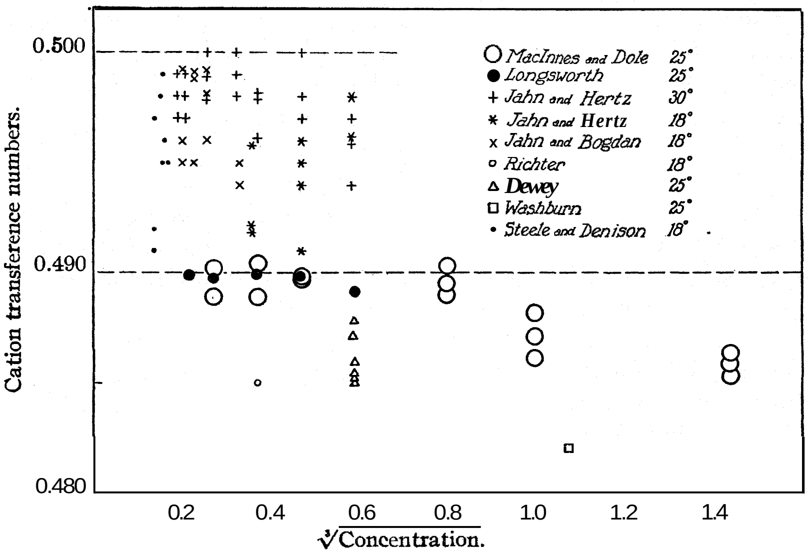

Fig. 3.

It is certainly evident from the discussion of our work and that of the previous investigators that it is difficult to obtain accurate transference numbers by the Hittorf method. Much higher precision can be obtained by the moving boundary method, and with relative ease. The width of the dots representing the moving boundary results in Fig. 3, illustrates roughly, on the scale of ordinates, the limits of error of these results. The value at each concentration represents the mean of at least four determinations, the deviation being 0.05% at most. Furthermore, fifteen figures which are averaged are obtained in each determination, the greatest variation being about 0.1%. Three complete determinations may be carried out in one day. A Hittorf determination which, if successful, gives one figure each for the anode and cathode portions, requires nearly a week.

On the other hand, the theory underlying the Hittorf measurements is simpler than that of the moving boundary method. Since the results of the latter method have been questioned recently,[11] the agreement of the results of these two accurate series of determinations is welcome.

The transference numbers of potassium chloride have been universally used in computing tables of limiting ion mobilities. The results given above indicate that the figures in those tables must be in error. A later paper from this Laboratory will deal with the determination of a new table of those constants based on recent conductance and transference data and on modern theories of solutions of strong electrolytes.

Summary

A series of measurements, by the Hittorf method, of the transference numbers of potassium chloride, at 25°, for the concentration range 0.02 to 3 normal is described. The cation transference numbers are decidedly lower than the generally accepted values for these constants, on which the tables of ionic mobilities are based. The new values are, however, in excellent agreement with a series of values for the same constants obtained by the moving boundary method, the details of the determinations of which will be published later.

Within the experimental error the transference numbers are constant between 0.01 and 0.1 *N* and the cation number decreases slowly above the latter concentration.

NEW YORK, N. Y.

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[11] Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., 2d ed., 1931, p. 685; also Mukherjee, *Nature*, **122**, 608 (1928); *J. Indian Chem. Soc.*, **5**, 593 (1928). This author considers that there is a large space charge at a moving boundary which appreciably affects its motion. This, he thinks, is caused by the sudden change of the transference number of the common ion at the plane of the boundary. It can readily be shown (though it would lead us too far afield at this point) that this supposed effect is due to a neglect of the fact that the boundary *moves*, the apparent deficiency in the number of the common ions behind the boundary being accounted for by a change of concentration of the ion as the boundary passes a given point.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

THE CONSTRUCTION OF DEWAR FLASKS

BY T. E. PHIPPS, M. J. COPLEY AND E. J. SHAW

RECEIVED FEBRUARY 10, 1931 PUBLISHED APRIL 6, 1931

A method of making Pyrex Dewar flasks of considerable capacity has been developed which may be of interest to some who have a limited or intermittent supply of liquid air. The most convenient size, in view of the limited sizes of Pyrex flasks, is probably three liters. The outer wall is made of a 5-liter flask. If 7- or 8-liter flasks were available, 5-liter Dewars could be constructed. However, with a 12-liter outer flask, silvering becomes rather difficult, and the resulting flask is too bulky to be practical.

A heavy-walled 16-mm. tube, E in the figure, is sealed to the base of the neck of a 5-liter round-bottomed flask. The heavy ring at the top of the neck is then cut off as closely as possible and the flask cut in two parts around a great circle perpendicular to the axis of the neck. The crack is shown at B. It is made by scratching a file mark about an inch long on the flask, wrapping one turn of No. 22 chrome1 wire about the flask, and heating with a current of 10–12 amp. until the glass is felt to be warm 6–8 mm. from the wire. A few cc. of water is poured on the file mark. The crack obtained is often so smooth that there is difficulty in determining the relative positions previous to cracking. The inner flask is prepared by cutting off the neck of a 3-liter flask as closely as possible to the base of the neck, A, and sealing on a previously flared 40-mm. heavy-walled tube. This is then cut off so that it extends through the neck of the outer flask a distance about equal to that between the walls of the neck.

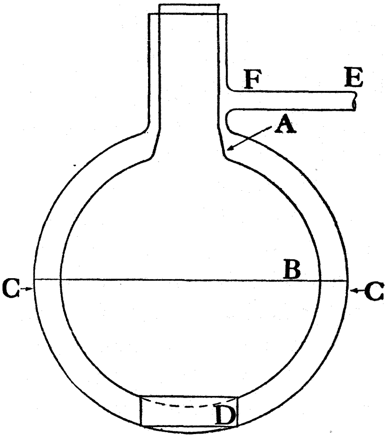

Fig. 1.

The bottom half of the outer flask is placed in an asbestos-covered iron ring. A ring of brass, D, such as a 20-mm. length of a 70-mm. brass tube is then placed in the glass hemisphere, and the inner flask is set on it. The upper half of the outer flask is put in place and clamped down with another asbestos-covered iron ring. The Dewar seal at the top is then made using two hand torches, one with a large air–gas flame, the other with a moderate air-oxygen–gas flame. Obviously this must be done at a rather high temperature, since the inner flask is essentially unstable. Blowing can be done through the evacuating tube, but is usually unnecessary.

Keeping the Dewar seal just below the softening point, the upper iron ring is removed, then the inner flask and top half of the outer lifted and the brass ring removed. The upper half is then replaced, and a large ring burner with holes every 8 mm. is placed around the whole just below the crack, at C. A small gas flame is started first, and the temperature raised slowly. When near the softening point, a small oxyhydrogen torch is used to make the large seal. About four points around the circumference should be sealed initially and then the seal completed rather than attempting to work right around.

As soon as the seal is completed the ring burner is removed and the entire ring stand put in an electric furnace at a temperature of about 600°. The Dewar seal should be at annealing temperature before this transfer is made. The furnace temperature is maintained for about an hour and then the current turned off. After two or three hours the cover is removed and the flask taken out when the furnace is cold.

If new flasks are used it is unnecessary to clean them with cleaning solution, but they should be washed with stannous chloride, rinsed and silvered. Rinsing and silvering should be done with a small quantity of liquid, by shaking and rotating, rather than filling the entire space between the walls. Two or three coats of silver are desirable. The silver is then washed out of the evacuating tube with cotton soaked with very dilute nitric acid, the entire flask rinsed several times with water, and the evacuating tube necked down at F for sealing off. Evacuation is carried out at about 400° in the electric furnace over a period of thirty-six hours, by means of a mercury vapor pump and liquid-air trap. Evacuation for a shorter period of time fails to outgas the silver completely and the flask deteriorates rather rapidly. Sealing off is done as soon after turning off the heat as possible. Our practice is to anneal two of the Dewar flasks at once (this requires the moving of one while hot from one ring stand to another already in the furnace) and later to evacuate them together.

The flask is ordinarily packed in Sil-O-Cel in a 12- or 14-quart pail, and covered over with heavy felt in which a hole is cut for the neck.

One of these Dewars, if filled with liquid air and set aside, will still contain some at the end of thirteen days, whereas the best commercial glass Dewars are empty in four days or less. Also, the soft glass Dewars ordinarily used usually last less than twenty fillings. One of our Pyrex Dewars has been in continuous use for more than three years, and still keeps liquid air as well as it ever did.

URBANA, ILLINOIS

[Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 280]

THE NATURE OF THE CHEMICAL BOND. APPLICATION OF RESULTS OBTAINED FROM THE QUANTUM MECHANICS AND FROM A THEORY OF PARAMAGNETIC SUSCEPTIBILITY TO THE STRUCTURE OF MOLECULES

By Linus Pauling

Received February 17, 1931 Published April 6, 1931

During the last four years the problem of the nature of the chemical bond has been attacked by theoretical physicists, especially Heitler and London, by the application of the quantum mechanics. This work has led to an approximate theoretical calculation of the energy of formation and of other properties of very simple molecules, such as H_2, and has also provided a formal justification of the rules set up in 1916 by G. N. Lewis for his electron-pair bond. In the following paper it will be shown that many more results of chemical significance can be obtained from the quantum mechanical equations, permitting the formulation of an extensive and powerful set of rules for the electron-pair bond supplementing those of Lewis. These rules provide information regarding the relative strengths of bonds formed by different atoms, the angles between bonds, free rotation or lack of free rotation about bond axes, the relation between the quantum numbers of bonding electrons and the number and spatial arrangement of the bonds, etc. A complete theory of the magnetic moments of molecules and complex ions is also developed, and it is shown that for many compounds involving elements of the transition groups this theory together with the rules for electron-pair bonds leads to a unique assignment of electron structures as well as a definite determination of the type of bonds involved.[1]

I. The Electron-Pair Bond

The Interaction of Simple Atoms.—The discussion of the wave equation for the hydrogen molecule by Heitler and London,[2] Sugiura,[3] and Wang[4] showed that two normal hydrogen atoms can interact in either of two ways, one of which gives rise to repulsion with no molecule formation, the other

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[1] A preliminary announcement of some of these results was made three years ago [Linus Pauling, *Proc. Nat. Acad. Sci.*, 14, 359 (1928)]. Two of the results (90° bond angles for p eigenfunctions, and the existence, but not the stability, of tetrahedral eigenfunctions) have been independently discovered by Professor J. C. Slater and announced at meetings of the National Academy of Sciences (Washington, April, 1930) and the American Physical Society (Cleveland, December, 1930).

[2] W. Heitler and F. London, *Z. Physik*, 44, 455 (1927).

[3] Y. Sugiura, *ibid.*, 45, 484 (1927).

[4] S. C. Wang, *Phys. Rev.*, 31, 579 (1928).

to attraction and the formation of a stable molecule. These two modes of interaction result from the identity of the two electrons. The characteristic resonance phenomenon of the quantum mechanics, which produces the stable bond in the hydrogen molecule, always occurs with two electrons, for even though the nuclei to which they are attached are different, the energy of the unperturbed system with one electron on one nucleus and the other on the other nucleus is the same as with the electrons interchanged. Hence we may expect to find electron-pair bonds turning up often.

But the interaction of atoms with more than one electron does not always lead to molecule formation. A normal helium atom and a normal hydrogen atom interact in only one way,[5] giving repulsion only, and two normal helium atoms repel each other except at large distances, where there is very weak attraction.[5,6] Two lithium atoms, on the other hand, can interact in two ways,' giving a repulsive potential and an attractive potential, the latter corresponding to formation of a stable molecule. In these cases it is seen that only when each of the two atoms initially possesses an unpaired electron is a stable molecule formed. The general conclusion that an electron-pair bond is formed by the interaction of an unpaired electron on each of two atoms has been obtained formally by Heitler[8] and London,[9] with the use of certain assumptions regarding the signs of integrals occurring in the theory. The energy of the bond is largely the resonance or interchange energy of two electrons. This energy depends mainly on electrostatic forces between electrons and nuclei, and is not due to magnetic interactions, although the electron spins determine whether attractive or repulsive potentials, or both, will occur.

Properties of the Electron-Pair Bond.—From the foregoing discussion we infer the following properties of the electron-pair bond.

1. *The electron-pair bond is formed through the interaction of an unpaired electron on each of two atoms.*

2. *The spins of the electrons are opposed when the bond is formed, so that they cannot contribute to the paramagnetic susceptibility of the substance.*

3. *Two electrons which form a shared pair cannot take part in forming additional pairs.*

In addition we postulate the following three rules, which are justified by the qualitative consideration of the factors influencing bond energies. An outline of the derivation of the rules from the wave equation is given below.

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[5] G. Gentile, *Z. Physik.*, 63, 795 (1930).

[6] J. C. Slater, *Phys. Rev.*, 32, 349 (1927).

[7] M. Delbrück, *Ann. Physik*, 5, 36 (1930).

[8] W. Heitler, *Z. Physik*, 46, 47 (1927); 47, 835 (1928); *Physik. Z.*, 31, 185 (1930), etc.

[9] F. London, *Z. Physik*, 46, 455 (1928); *50*, 24 (1928); "Sommerfeld Festschrift," p. 104; etc.

4. *The main resonance terms for a single electron-pair bond are those involving only one eigenfunction from each atom.*

5. *Of two eigenfunctions with the same dependence on r, the one with the larger value in the bond direction will give rise to the stronger bond, and for a given eigenfunction the bond will tend to be formed in the direction with the largest value of the eigenfunction.*

6. *Of two eigenfunctions with the same dependence on θ and φ, the one with the smaller mean value of r, that is, the one corresponding to the lower energy level for the atom, will give rise to the stronger bond.*

Here the eigenfunctions referred to are those for an electron in an atom, and r, θ and φ are polar coordinates of the electron, the nucleus being at the origin of the coordinate system.

It is not proposed to develop a complete proof of the above rules at this place, for even the formal justification of the electron-pair bond in the simplest cases (diatomic molecule, say) requires a formidable array of symbols and equations. The following sketch outlines the construction of an inclusive proof.

It can be shown[10] that if Ψ is an arbitrary function of the independent variables in a wave equation

$$(H - W)\psi = 0$$

then the integral

$$E = \int \Psi^* H \Psi d\tau$$

called the variation integral, is always larger than W_0, the lowest energy level for the system. A function Ψ containing several parameters provides the best approximation to the eigenfunction ψ_0 for the normal state of the system when the variational integral is minimized with respect to these parameters. Now let us consider two atoms A and B connected by an electron-pair bond, and for simplicity let all the other electrons in the system be paired, the pairs being either lone pairs or pairs shared between A or B and other atoms. Let us assume that there are available for bond formation by atom A several single-electron eigenfunctions of approximately the same energy, and that the change in energy of penetration into the core is negligible compared with bond energy. Then we may take as single-electron eigenfunctions

$$\psi_{\mathrm{A}i} = \Sigma_k\, a_{ik}\, \psi^0_{\mathrm{A}k}$$

in which the a_{ik}'s are numerical coefficients and the $\psi^0_{\mathrm{A}k}$'s are an arbitrary set of single-electron eigenfunctions, such as those obtained on separating the wave equation in polar coordinates. From the $\psi_{\mathrm{A}i}$'s there is built up a group composed of atom A and the atoms to which it is bonded except atom B, such that all electrons are paired except one, corresponding to the eigenfunction $\psi_{\mathrm{A}i}$, say. From atom B a similar group with one unpaired electron is built. The interaction energy of these two groups can then be calculated with the aid of the variational equation through the substitution of an eigenfunction for the molecule built of those for the two groups in such a way that it has the correct symmetry character. The construction of this eingenfunetion and evaluation of the integral would be very laborious; it will be noticed, however, that this problem is formally similar to Born's treatment[11] of the interaction of two atoms in S states, based on Slater's treatment of atomic eigenfunctions, and the value of E is found to be

$$E = W_{\mathrm{A}} + W_{\mathrm{B}} + J_E + J_X - \Sigma_Y J_Y - 2\Sigma_Z J_Z$$

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[10] A clear discussion is given by C. Eckart, *Phys. Rev.*, 36, 878 (1930).

[11] M. Born, *Z. Physik*, 64, 729 (1930).

Here W_A and W_B are the energies of the separate groups, and J_E represents the Coulomb interaction of A and B, neglecting resonance. The resonance term J_X corresponds to a permutation of the two AB bond electrons; J_Y corresponds to a permutation of the AB bond electron on B with a paired electron with similarly directed spin on A, or *vice verso;* and J_Z corresponds to a permutation of a paired electron on A with one on B (For explicit expressions for these see Born.[11]) The resonance integrals J_X, J_Y and J_Z have been found to have negative signs in the case of simple molecules for which calculations have been made, and it is probable that these signs obtain in most cases. The resonance integrals depend qualitatively on what may be called the *overlapping* of the single-electron eigenfunctions involved; if ψ_A and ψ_B are two single-electron eigenfunctions, the product $\psi_A(1)\,\psi_B(2)\,\psi_A^*(2)\,\psi_B^*(1)$ occurs in the resonance integral corresponding to the permutation involving electrons 1 and 2, and the value of the integral increases as the magnitude of this product in the region between the two nuclei increases.

Now we vary the coefficients a_{ik} in such a way as to minimize E. W_A and W_B are not affected by this variation, and J_E is not changed in case that there is one electron for every eigenfunction in a subgroup on A, and is changed relatively slightly otherwise. The resonance integrals are, however, strongly affected by changing the coefficients. The positive sign preceding J_X requires that the two bond eigenfunctions ψ_A and ψ_B show the maximum overlapping in the region between the two nuclei, while the negative sign preceding J_Y requires the minimum overlapping between ψ_A and the eigenfunctions of B other than ψ_B, and between ψ_B and the eigenfunctions of A other than ψ_A. Hence the correct zeroth-order eigenfunctions for the atom A are such that one, the AB bond eigenfunction ψ_A, extends largely in the direction of atom B, while the other A eigenfunctions avoid overlapping with ψ_B. As a consequence the integral J_X is of large magnitude, while the integrals J_Y, because of the small overlapping of the eigenfunctions involved, are small.

An extension of this argument shows that the phenomenon of *concentration of the bond eigenfunctions* further increases the magnitude of J_X and decreases J_Y. The nonorthogonality of the bond eigenfunctions as well as certain second-order perturbations leads to a shrinkage of the region in which the bond eigenfunctions have appreciable values. This is strikingly shown by a comparison of H_2^+ and H; the volume within which the electron probability function $\psi\psi^*$ for H_2^+ is greater than one-tenth of its maximum value is found from Burrau's calculations to be 0.67 $Å.^3$, less than 10% of its value 8.6 $Å.^3$ for a hydrogen atom.[12] This concentration of the bond eigenfunctions greatly increases their interaction with one another, and decreases their interaction with other eigenfunctions, a fact expressed in Rule 4. For double or triple bonds interactions among all four or six eigenfunctions must be considered.

s and *p* Eigenfunctions. Compounds of Normal Atoms.—As a rule s and *p* eigenfunctions with the same total quantum number in an atom do not differ very much in their mean values of r (the s levels lie lower because of greater penetration of inner shells), so that Rule 6 would not lead us to expect them to differ in bond-forming power. But their dependence on θ and φ is widely different. Putting

$$\begin{aligned} \Psi_{n0}(r,\theta,\varphi) &= R_{n0}(r)\cdot s(\theta,\varphi) && \text{for } s \text{ eigenfunctions} \\ \Psi_{n1}(r,\theta,\varphi) &= R_{n1}(r)\cdot \left.\begin{matrix} p_x(\theta,\varphi) \\ p_y(\theta,\varphi) \\ p_z(\theta,\varphi) \end{matrix}\right\} && \text{for } p \text{ eigenfunctions} \end{aligned} \qquad (1)$$

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[12] Compare Fig. 6 with Fig. 7, which is drawn to half the scale of Fig. 6, of Linus Pauling, *Chem. Rev.*, 5, 173 (1928).

the parts s, p_x, p_y, p_z of the eigenfunctions depending on θ and φ, normalized to 4π, are

$$\left.\begin{aligned} s &= l \\ p_x &= \sqrt{3}\sin\theta\cos\varphi \\ p_y &= \sqrt{3}\sin\theta\sin\varphi \\ p_z &= \sqrt{3}\cos\theta \end{aligned}\right\} \qquad (2)$$

Absolute values of s and p_x are represented in the xz plane in Figs. 1 and 2. s is spherically symmetrical, with the value 1 in all directions. $|p_x|$ consists of two spheres as shown (the x axis is an infinite symmetry axis), with the maximum value $\sqrt{3}$ along the x axis. $|p_y|$ and $|p_z|$ are similar, with maximum values of $\sqrt{3}$ along the y and z axis, respectively. From Rule 5 we conclude that *p electrons will form stronger bonds than s electrons*, and that *the bonds formed by p electrons in an atom tend to be oriented at right angles to one another.*

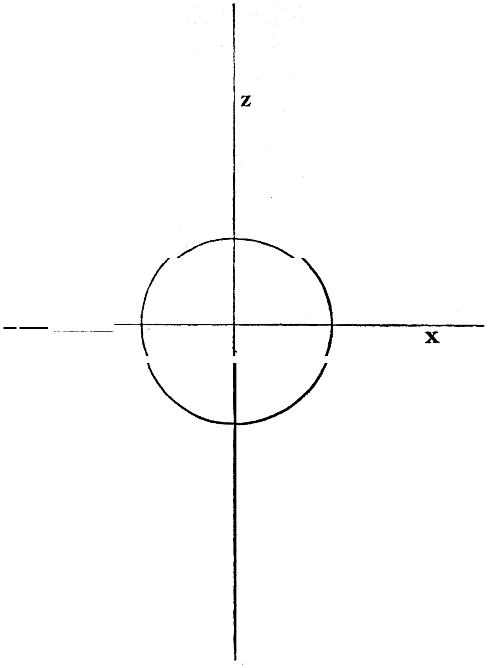
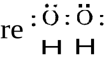


Fig. 1.—Polar graph of 1 in the xz plane, representing an s eigenfunction.

The second conclusion explains several interesting facts. Normal oxygen, in the state $2s^22p^4\ {}^3P$, contains two unpaired p electrons. When an atom of oxygen combines with two of hydrogen, a water molecule will result in which the angle formed by the three atoms is 90°, or somewhat larger because of interaction of the two hydrogen atoms. It has been long known from their large electric moment that water molecules have a kinked rather than a collinear arrangement of their atoms, and attempts have been made to explain this with rather unsatisfactory calculations based on an ionic structure with strong polarization of the oxygen anion in the field of the protons. The above simple explanation results directly from the reasonable assumption of an electron-pair bond structure and the properties of tesseral harmonics.

It can be predicted that H_2O_2, with the structure  $:\ddot{\underset{H}{O}}:\ddot{\underset{H}{O}}:$ involving bonds of p electrons, also consists of kinked rather than collinear molecules.

Nitrogen, with the normal state $2s^22p^S\ {}^4S$, contains three unpaired p electrons, which can form bonds at about 90° from one another with three hydrogen atoms. The ammonia molecule, with the resulting pyramidal structure, also has a large electric moment.

The crystal skutterudite, $Co_4^{3+}(As_4^{4-})_3$, contains As_4^{4-} groups with a square configuration, corresponding to the structure $\left[\begin{matrix}:\ddot{As}:As:\\ :\underset{..}{\ddot{As}}:\underset{..}{\ddot{As}}:\end{matrix}\right]^{4-}$. This complex has bond angles of exactly 90°.

In the above discussion it has been assumed that the type of quantization has not been changed, and that *s* and *p* eigenfunctions retain their identity. This is probably true for H_2O and H_2O_2, and perhaps for NH_3 and As_4^{4-} also. A discussion of the effect of change of quantization on bond angles is given in a later section.

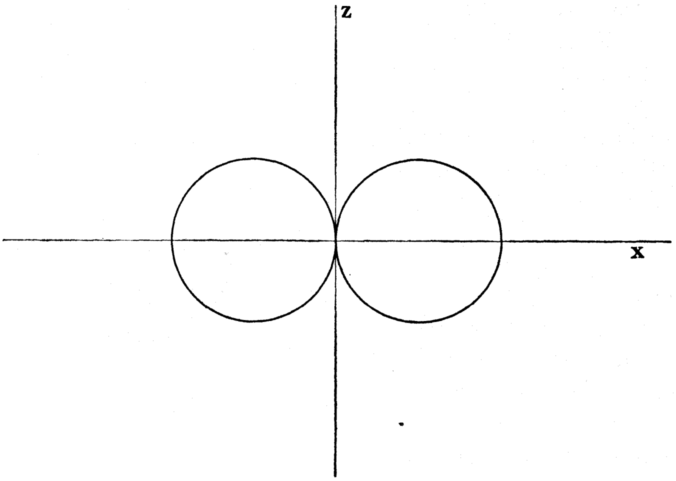


Fig. 2.—Polar graph of $|\sqrt{3}\sin\theta|$ in the xz plane, representing the p_x eigenfunction.

Transition from Electron-Pair to Ionic Bonds. The Hydrogen Bond.—In case that the symmetry character of an electron-pair structure and an ionic structure for a molecule are the same, it may be difficult to decide between the two, for the structure may lie anywhere between these extremes. The zeroth-order eigenfunction for the two bond electrons for a molecule MX (HF, say, or NaCl) with a single electron-pair bond would be

$$\Psi_{MX} = \frac{\psi_M(1)\,\psi_X(2) + \psi_M(2)\,\psi_X(1)}{\sqrt{2+2S^2}} \qquad (3)$$

in which $S = \int \psi_M(1)\,\psi_X^*(1)\,d\tau_1$. The eigenfunction for a pure ionic state would be

$$\Psi_{M^+X^-} = \psi_X(1)\,\psi_X(2) \qquad (4)$$

In certain cases one of these might approximate the correct eigenfunction closely. In other cases, however, it would be necessary to consider combinations of the two, namely

$$\Psi_+ = a\,\Psi_{MX} + \sqrt{1-a^2}\,\Psi_{M^+X^-}$$

and

$$\Psi_- = \sqrt{1-a^2}\,\Psi_{MX} - a\,\Psi_{M^+X^-} \qquad (5)$$

For a given molecule and a given internuclear separation a would have a definite value, such as to make the energy level for Ψ_+ lie as low as possible. If a happens to be nearly 1 for the equilibrium state of the molecule, it would be convenient to say that the bond is an electron-pair bond; if a is nearly zero, it could be called an ionic bond. This definition is somewhat unsatisfactory in that it does not depend on easily observable quantities. For example, a compound which is ionic by the above definition might dissociate adiabatically into neutral atoms, the value of a changing from nearly zero to unity as the nuclei separate, and it would do this in case the electron affinity of X were less than the ionization potential of M. HF is an example of such a compound. There is evidence, given below, that the normal molecule approximates an ionic compound; yet it would dissociate adiabatically into neutral F and H.[13]

But direct evidence regarding the value of a can sometimes be obtained. The hydrogen bond, discovered by Huggins and by Latimer and Rodebush, has been usually considered as produced by a hydrogen atom with two electron-pair bonds, as in $\left[:\overset{..}{\underset{..}{F}}:H:\overset{..}{\underset{..}{F}}:\right]^-$. It was later pointed out[1] that this is not compatible with the quantum mechanical rules, for hydrogen can have only one unpaired 1s electron, and outer orbits are so much less stable that strong bonds would not be formed. With an ionic structure, however, we would expect H^+F^- to polymerize and to add on to F^-, to give H_6F_6 and $[F^-H^+F^-]^-$; moreover, the observed coordination number 2 is just that predicted[14] from the radius ratio 0. Hence the observation that hydrogen bonds are formed with fluorine supports an ionic structure for HF. Hydrogen bonds are not formed with chlorine, bromine, and iodine, so that the bonds in HCl, HBr, and HI are to be considered as approaching the electron-pair type.

Hydrogen bonds are formed to some extent by oxygen ($(H_2O)_x$, ice, etc.) and perhaps also in some cases by nitrogen. The electrostatic structure for the hydrogen bond explains the observation that only these atoms of high electron affinity form such bonds, a fact for which no explanation was given by the older conception. It is of interest that there is considerable

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[13] There would, however, be a certain probability, dependent on the nature of the eigenfunctions, that actual non-adiabatic dissociation would give ions rather than atoms, and this might be nearly unity, in case the two potential curves come very close to one another at some point. See I. v. Neumann and E. Wigner. *Physik.* Z.. 30, 467 (1929).

[14] Linus Pauling, THIS JOURNAL, 51, 1010 (1929).

evidence from crystal structure data for [OHO]' groups. In many crystals containing H and O, including topaz,[15] $Al_2SiO_4(F,OH)_2$; diaspore,[16] $AlHO_2$; goethite,[16] $FeHO_2$; chondrodite,[17] $Mg_5Si_2O_8(F,OH)_2$; etc., the sum of the strengths of the electrostatic bonds from all cations (except hydrogen) to an anion is either 2 or 1, indicating, according to the electrostatic valence rule,[14] the presence of $O^=$ and of F^- or $(OH)^-$, respectively. But in some crystals, including[18] KH_2PO_4; staurolite,[19] $H_2FeAl_4Si_2O_{12}$; and lepidocrocite,[16] $FeHO_2$, the sum of bond strengths is 2 or $^3/_2$, the latter value occurring twice for each H; the electrostatic valence rule in these cases supports the assumption of $[O^=H^+O^=]^\equiv$ groups, the hydrogen ion contributing a bond of strength $^1/_2$ to each of two oxygen ions.

In other cases, discussed below, the lowest electron-pair-bond structure and the lowest ionic-bond structure do not have the same multiplicity, so that (when the interaction of electron spin and orbital motion is neglected) these two states cannot be combined, and a knowledge of the multiplicity of the normal state of the molecule or complex ion permits a definite statement as to the bond type to be made.

Change in Quantization of Bond Eigenfunctions.—A normal carbon atom, in the state $2s^22p^2$ ^3P, contains only two unpaired electrons, and can hence form no more than two single bonds or one double bond (as in CO, formed from a normal carbon atom and a normal oxygen atom). But only about 1.6 v. e. of energy is needed to excite a carbon atom to the state $2s2p^3$ ^5S, with four unpaired electrons, and in this state the atom can form four bonds. We might then describe the formation of a substituted methane CRR′R″R‴ in the following way. The radicals R, R′, and R″, each with an unpaired electron, form electron-pair bonds with the three *p* electrons of the carbon atom, the bond directions making angles of 90° with one another. The fourth radical R‴ then forms a weaker bond with the *s* electron, probably at an angle of 125° with each of the other bonds. This would give an unsymmetrical structure, with non-equivalent bonds, and considerable discussion has been given by various authors to the difference in the carbon bonds due to *s* and *p* electrons. Actually the foregoing treatment is fallacious, for the phenomenon of change in quantization of the bond eigenfunctions, first discussed in the note referred to before,' leads simply and directly to the conclusion that ***the four bonds formed by a carbon atom are equivalent and are directed toward tetrahedron corners.***

The importance of *s*, *p*, d, and f eigenfunctions for single atoms and ions

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[15] Linus Pauling, *Proc. Nat. Acad. Sci.*, 14, 603 (1928); N. A. Alston and J. West, *Z. Krist.*, 69, 149 (1928).

[16] Unpublished investigation in this Laboratory.

[17] W. L. Bragg and J. West, *Proc. Roy. Soc.* (London). A114, 450 (1927); W. H. Taylor and J. West, *ibid.*, A117, 517 (1928).

[18] J. West, *Z. Krist.*, 74, 306 (1930).

[19] St. Naray-Szabo, *ibid.*, 71, 103 (1929).

results from the fact that the interaction of one electron with the nucleus and other electrons can be represented approximately by a non-Coulombian central field, so that the wave equation can be separated in polar coordinates r, θ, and φ, giving rise to eigenfunctions involving tesseral harmonics such as those in Equation 1. The deeper penetration of s electrons within inner shells causes them to be more tightly bound than p electrons with the same total quantum number. If an atom approaches a given atom, forming a bond with it, the interaction between the two can be considered as a perturbation, and the first step in applying the perturbation theory for a degenerate system consists in finding the correct zeroth-order eigenfunctions for the perturbation, one of which is the eigenfunction which will lead to the largest negative perturbation energy. This will be the one with the largest values along the bond direction. The correct zeroth-order eigenfunctions must be certain normalized and mutually orthogonal linear aggregates of the original eigenfunctions. If the perturbation is small, the s eigenfunction cannot be changed, and the only combinations which can be made with the p eigenfunctions are equivalent merely to a rotation of axes. But in case the energy of interaction of the two atoms is greater than the difference in energy of an s electron and a p electron (or, if there are originally two s electrons present, as in a normal carbon atom, of twice this difference), hydrogen-like s and p eigenfunctions must be grouped together to form the original degenerate state, and the interaction of the two atoms together with the deviation of the atomic field from a Coulombian one must be considered as the perturbation, with the former predominating. The correct zeroth-order bond eigenfunctions will then be those orthogonal and normalized linear aggregates of both the s and p eigenfunctions which would give the strongest bonds according to Rule 5.

A rough criterion as to whether the quantization is changed from that in polar coordinates to a type giving stronger bond eigenfunctions is thus that the possible bond energy be greater than the s–p (or, if d eigenfunctions are also involved, s–d or p–d) separation.[20]

This criterion is satisfied for quadrivalent carbon. The energy difference of the states[21] $2s^22p^2\ ^3P$ and $2s2p^3\ ^3P$ of carbon is 9.3 v. e., and a similar value of about 200,000 cal. per mole is found for other atoms in the first row of the periodic system. The energy of *a* single bond is of the order of 100,000 cal. per mole. Hence a carbon atom forming four bonds would certainly have changed quantization, and even when the bond energy must be divided between two atoms, as in a diamond crystal, the criterion is sufficiently well satisfied. The same results hold for quadrivalent

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[20] This criterion was expressed in Ref. 1.

[21] States with the same multiplicity should be compared, for increase in multiplicity decreases the term value, the difference between $2s^22p^2\ ^3P$ and $2s2p^3\ ^5S$ being only about 1.6 v. e., as mentioned above.

nitrogen, a nitrogen ion in the state N^+ $2s2p^3$ ^5S forming four bonds, as in $(NH_4)^+$, $N(CH_3)_4{}^+$, etc. But for bivalent oxygen there is available only about 200,000 cal. per mole bond energy, and the *s–p* separation for two *s* electrons corresponds to about 400,000 cal. per mole, so that it is very probable that the oxygen bond eigenfunctions in H_2O, for example, are *p* eigenfunctions, as assumed in a previous section. Trivalent nitrogen is a border-line case; the bond energy of about 300,000 cal. per mole is sufficiently close to the *s–p* energy of 400,000 cal. per mole to permit the eigenfunctions to be changed somewhat, but not to the extent that they are in quadrivalent carbon and nitrogen.

It may be pointed out that the *s–p* separation for atoms in the same column of the periodic table is nearly constant, about 200,000 cal. per mole for one *s* electron. The bond energy decreases somewhat with increasing atomic number. Thus the energies of a bond in the compounds H_2O, H_2S, H_2Se, and H_2Te, calculated from thermochemical and band spectral data, are 110,000, 90,000, 73,000, and 60,000 cal. per mole, respectively. Hence we conclude that if quantization in polar coordinates is not broken for a light atom on formation of a compound, it will not be broken for heavier atoms in the same column of the periodic system. The molecules HS, H_2Se, and H_2Te must accordingly also have a non-linear structure, with bond angles of 90° or slightly greater.

Let us now determine the zeroth-order eigenfunctions which will form the strongest bonds for the case when the *s–p* quantization is broken. The dependence on *r* of *s* and *p* hydrogen-like eigenfunctions is not greatly different,[22] and it seems probable that the effect of the non-Coulombian field would decrease the difference for actual atoms. We may accordingly assume that $R_{n0}(r)$ and $R_{n1}(r)$ are effectively the same as far as bond formation is concerned, so that the problem of determining the bond eigenfunctions reduces to a discussion of the 6, φ eigenfunctions of Equation 1. Arbitrary sets of 6, φ eigenfunctions formed from s, p_x, p_y, and p_z are given by the expressions

$$\left.\begin{aligned} \psi_1 &= a_1s + b_1p_x + c_1p_y + d_1p_z \\ \psi_2 &= a_2s + b_2p_x + c_2p_y + d_2p_z \\ \psi_3 &= a_3s + b_3p_x + c_3p_y + d_3p_z \\ \psi_4 &= a_4s + b_4p_x + c_4p_y + d_4p_z \end{aligned}\right\} \qquad (6)$$

in which the coefficients a_1, etc., are restricted only by the orthogonality and normalization requirements

$$\int \psi_i^2 d\tau = 1 \quad \text{or } a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1 \qquad i = 1,2,3,4 \qquad (7a)$$

and

$$\int \psi_i\psi_k d\tau = 0 \quad \text{or } a_ia_k + b_ib_k + c_ic_k + d_id_k = 0 \quad i,k = 1,2,3,4 \quad i \neq k \qquad (7b)$$

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[22] **See the curves given by Linus Pauling, *Proc. Roy. Soc.* (London). A114, 181 (1927), or A. Sommerfeld, "Wellenmechanischer Erganzungsband," p. 88.**

From Rule 5 the best bond eigenfunction will be that which has the largest value in the bond direction. This direction can be chosen arbitrarily for a single bond. Taking it along the *x* axis, it is found that the best single bond eigenfunction is[23]

$$\psi_1 = \frac{1}{2}s + \frac{\sqrt{3}}{2}p_x \tag{8a}$$

with a maximum value of 2, considerably larger than that 1.732 for a *p* eigenfunction. A graph of this function in the *xz* plane is shown in Fig. **3.**

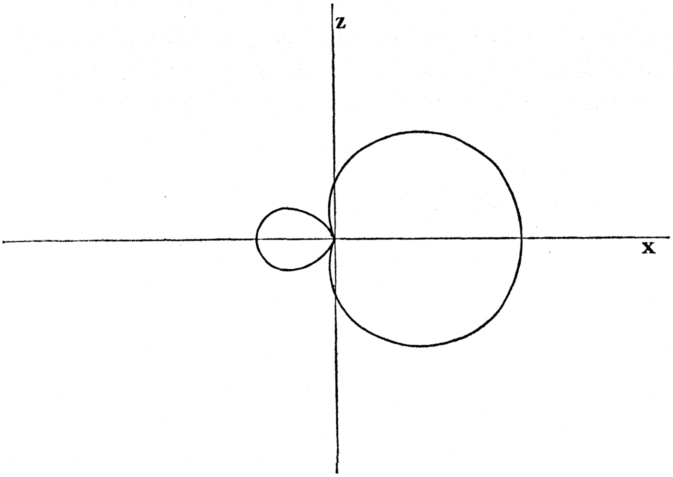

Fig. 3.—Polar graph of $\left| {}^1/_2 + {}^3/_2 \sin \theta \right|$ in the *xz* plane, representing a tetrahedral eigenfunction, the best bond eigenfunction which can be formed from *s* and *p* eigenfunctions.

A second bond can be introduced in the *xz* plane. The best eigenfunction for this bond is found to be

$$\psi_2 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x + \frac{\sqrt{2}}{\sqrt{3}}p_z \tag{8b}$$

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[23] It is easily shown with the use of the method of undetermined multipliers that the eigenfunction with the maximum value in the direction defined by the polar angles θ_0, φ_0 has as coefficients of the initial eigenfunctions quantities proportional to $\psi_k(\theta_0,\varphi_0)$, and that the maximum value is itself equal to $\{\Sigma_k[\psi_k(\theta_0,\varphi_0)]^2\}^{1/2}$. For let $\psi(\theta,\varphi) = \Sigma_{k=1}^{n} a_k\psi_k(\theta,\varphi)$, with $\Sigma a_k^2 = 1$. We want $\psi(\theta_0,\varphi_0) = \Sigma a_k\psi_k(\theta_0,\varphi_0)$ to ***be a*** maximum with respect to variation in the *a*, 's. Consider the expression

$$\Lambda = \psi(\theta_0,\varphi_0) - \frac{\lambda}{2}\{\Sigma a_k^2 - 1\} = \Sigma\left\{a_k\psi_k(\theta_0,\varphi_0) - \frac{\lambda}{2}a_k^2\right\} + \frac{X}{2}$$

in **which** λ is an undetermined multiplier. Then we put

$$\frac{\partial\Lambda}{\partial a_k} = \psi_k(\theta_0,\varphi_0) - \lambda a_k = 0 \text{ or } a_k = \frac{\psi_k(\theta_0,\varphi_0)}{\lambda},\ k = 1,2\ldots n$$

in which X has such a value that $\Sigma a_k^2 = 1$; *i. e.*, $\lambda = \{\Sigma[\psi_k(\theta_0,\varphi_0)]^2\}^{1/2}$. $\psi(\theta_0,\varphi_0)$ is itself then equal to $\Sigma[\psi_k(\theta_0,\varphi_0)]^2/\lambda$ or $\{\Sigma[\psi_k(\theta_0,\varphi_0)]^2\}^{1/2}$.

This eigenfunction is equivalent to and orthogonal to ψ_1, and has its maximum value of 2 at $\theta = 19°28'$, $\varphi = 180°$, that is, at an angle of 109°28' with the first bond, *which is just the angle between the lines drawn from the center to two corners of a regular tetrahedron.* The third and fourth best bond eigenfunctions

$$\psi_3 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_z - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y \tag{8c}$$

and

$$\psi_4 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_z - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y \tag{8d}$$

are also equivalent to the others, and have their maximum values of 2 along the lines toward the other two corners of a regular tetrahedron.

An equivalent set of four tetrahedral eigenfunctions is[24]

$$\left.\begin{aligned}
\psi_{111} &= \frac{1}{2}(s + p_x + p_y + p_z) \\
\psi_{1\bar{1}\bar{1}} &= \frac{1}{2}(s + p_x - p_y - p_z) \\
\psi_{\bar{1}1\bar{1}} &= \frac{1}{2}(s - p_x + p_y - p_z) \\
\psi_{\bar{1}\bar{1}1} &= \frac{1}{2}(s - p_x - p_y + p_z)
\end{aligned}\right\} \tag{9}$$

These differ from the others only by a rotation of the atom as a whole.

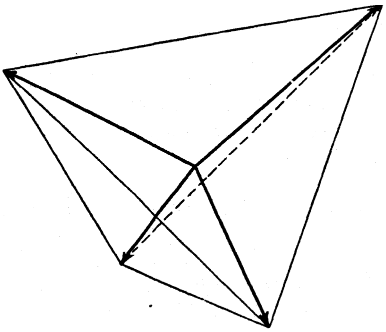

Fig. 4.—Diagram showing relative orientation in space of the directions of the maxima of four tetrahedral eigenfunctions.

The Tetrahedral Carbon Atom.—We have thus derived the result that *an atom in which only s and p eigenfunctions contribute to bond formation and in which the quantization in polar coördinates is broken can form one, two, three, or four equivalent bonds, which are directed toward the corners of a regular tetrahedron* (Fig. 4). This calculation provides the quantum mechanical justification of the chemist's tetrahedral carbon atom, present in diamond and all aliphatic carbon compounds, and for the tetrahedral quadrivalent nitrogen atom, the tetrahedral phosphorus atom, as in phosphonium compounds, the tetrahedral boron atom in B_2H_6 (involving single-electron bonds), and many other such atoms.

Free or Restricted Rotation.—Each of these tetrahedral bond eigen-

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[24] It should be borne in mind that the bond eigenfunctions actually are obtained from the expressions given in this paper by substituting for s the complete eigenfunction $\Psi_{n00}(r,\theta,\varphi)$, etc. It is not necessary that the r part of the eigenfunctions be identical; the assumption made in the above treatment is that they do not affect the evaluation of the coefficients in the bond eigenfunctions.

functions is cylindrically symmetrical about its bond direction. Hence the bond energy is independent of orientation about this direction, so that there will be *free rotation about a single bond,* except in so far as rotation is hindered by steric effects, arising from interactions of the substituent atoms or groups.

A double bond behaves differently, however. Let us introduce two substituents in the octants xyz and $\bar{x}\bar{y}z$ of an atom, a carbon atom, say, using the bond eigenfunctions ψ_{111} and $\psi_{\bar{1}\bar{1}1}$. The two eigenfunctions $\psi_{1\bar{1}\bar{1}}$ and $\psi_{\bar{1}1\bar{1}}$ are then left to form a double bond with another such group. Now $\psi_{1\bar{1}\bar{1}}$ and $\psi_{\bar{1}1\bar{1}}$ (or any two eigenfunctions formed from them) are not cylindrically symmetrical about the z axis or any direction, nor are the two eigenfunctions on the other group. Hence the energy of the double bond will depend on the relative orientation of the two tetrahedral carbon atoms, and will be a maximum when the two sets of eigenfunctions show the maximum overlapping. This will occur when the two tetrahedral atoms share an edge (Fig. 5). Thus we derive the result, found long ago by chemists, that there are two stable states for a simple compound involving a double bond, a *cis* and a *trans* state, differing in orientation by 180°. *There is no free rotation about a double bond.*[25]

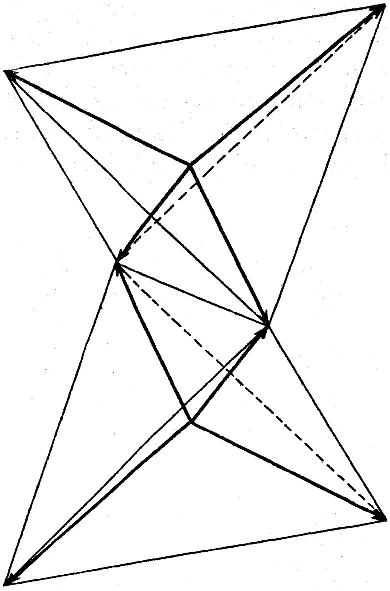

Fig. 5.—Directions of maxima of tetrahedral eigenfunctions in two atoms connected by a double bond.

The three eigenfunctions which would take part in the formation of a triple bond can be made symmetrical about the bond direction, for an atom of the type considered above, with only four eigenfunctions in the outer shell; but since the group attached by the fourth valence lies on the axis of the triple bond, there is no way of verifying the resulting free rotation about the triple bond.

The Angles between Bonds.—The above calculation of tetrahedral angles between bonds when the quantization is changed sets an upper limit on bond angles in doubtful cases, when the criterion is only approximately satisfied. For we can now state that the bond angles in H_2O and NH_3

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[25] A discussion of rotation about a double bond on the basis of the quantum mechanics has been published by E. Hückel, *Z. Physik,* 60, **423** (1930), which is, I feel, neither so straightforward nor so convincing as the above treatment, inasmuch as neither the phenomenon of concentration of the bond eigenfunctions nor that of change in quantization is taken into account.

should lie between 90 and 109°28′, closer to 90° for the first and to 109°28′ for the second compound. The same limits should apply to other atoms with an outer &shell (counting both shared and unshared electron pairs). Direct evidence on this point is provided by crystal structure data for non-ionic crystals, given in Table I. Every one of the angles given in this table depends on one or more parameters, which have been determined experimentally from observed intensities of x-ray reflections. The probable error in most cases is less than 5°, and in many is only about ±1°. It will be observed that quadrivalent carbon and nitrogen and trivalent nitrogen form bonds at tetrahedral angles, whereas heavier atoms forming only two or three bonds prefer smaller bond angles. The series As, Sb, Bi is particularly interesting. We expect, from an argument given earlier,

TABLE I

ANGLES BETWEEN BONDS, FROM CRYSTAL STRUCTURE DATA[a]

Compound	Atom	Number of bonds	Angles between bonds
$C_6N_4H_{12}$	C	2 C—N, 2 C—H	112° between C—N bonds
$C_6N_4H_{12}$	N	3 N—C	108°
$(NH_2)_2CO$[b]	C	2 single C—N 1 double C=O	115° between single bonds
As	As	3	97°
Sb	Sb	3	96°
Bi	Bi	3	94°
Se	Se	2	105°
Te	Te	2	102°
FeS_2[d] MnS_2 CoS_2 NiS_2	S^{++}	1 S—S 3 S—M	103° between S—S and S—M bonds 115° between two M—S bonds
MoS_2[e]	S^{+}	3 S—Mo	82°
$Co_4(As_4)_3$	As^{-}	2 As—AS	90°
$CaSi_2$	Si	3 Si—Si	103° between Si—Si bonds
HgI_2	I^{+}	2 Hg—I	103°
GeI_4	Ge	4 Ge—I	109.5°
SnI_4	Sn	4 Sn—I	109.5"
As_4O_6	As	3 As—O	109.5°
	O	20— As	109.5"
Sb_4O_6	Sb	3 Sb—O	109.5"
	O	20—Sb	109 5°
$NaClO_3$[c]	Cl^{++}	3 Cl—O	109 5°
$KClO_3$	Cl^{++}	3 Cl—O	109.5°
$KBrO_3$	Br^{++}	3Br—0	109.5"

[a] Data for which no reference is given are from the *Strukturbericht* of P. P. Ewald and C. Hermann. [b] R. W. G. Wyckoff, *Z. Krist.*, **75**, **529 (1930)**. [c] W. H. Zachariasen, *ibid.*, *71*, **501, 517 (1929)**. [d] The very small paramagnetic susceptibility of pyrite requires the presence of electron-pair bonds, eliminating an ionic structure $Fe^{++}S_2^{=}$. Angles are calculated for FeS_2, for which the parameters have been most accurately determined. [e] The parameter value (correct value u = **0.371)** and interatomic distances for molybdenite are incorrectly given in the *Strukturbericht.*

that the bond eigenfunctions will deviate less and less from pure *p* eigenfunctions in this order, and this evidences itself in a closer approach of the bond angle to 90° in the series. Geometrical effects sometimes affect the bond angles, as in As_4O_6 and Sb_4O_6, where a decrease in the oxygen bond angle would necessarily be accompanied by an increase in that for the other atom, and in molybdenite and pyrite.

Many compounds with tetrahedral structures (diamond, sphalerite, wurzite, carborundum, etc.) are known, in which the four bonds have tetrahedral angles. Tetrahedral atoms in such crystals include C (diamond, SiC), Si, Ge, Sn, Cl^{3+} (in CuCl), Br^{3*}, I^{3+}, O^{++} (in Cu_2O and ZnO), S^{-*}, Se^{++}, Te^{++}, N^{+} (in AlN), $P+$, $As+$, Sb^{+}, Bi^{+}, $Cu^{\equiv}$, $Zn^{=}$, $Cd^{=}$, $Hg^{=}$, PI–, Ga^{-} and In^{-}.

The Valence of Atoms.—In the last paragraph and in Table I the atoms are represented with electrical charges which are not those usually seen. These charges are obtained by the application of Rule 1, according to which an electron-pair bond is formed by one electron from each of the two atoms (even though as the atoms separate the type of bonding may change in such a way that both electrons go over to one atom). Accordingly in determining the state of ionization of the atoms in a molecule or crystal containing electron-pair bonds each shared electron-pair is to be split between the two atoms. In this way every atom is assigned an electrovalence obtained by the above procedure and a covalence equal to the number of its shared electron-pair bonds.

It is of interest to note that a quantity closely related to the "valence" of the old valence theory is obtained for an atom by taking the algebraic sum of the electrovalence and of the covalence, the latter being given the positive sign for metals and the negative sign for non-metals. For example, oxygen in OH^- is O^- with a covalence of 1, in H_2O it is O with a covalence of 2, in H_3O^+ it is Of with a covalence of **3,** and in crystalline ZnO it is O^{++} with a covalence of 4; in each case the above rule gives -2 for its valence.

Trigonal Quantization.--We have seen that an atom with *s-p* quantization unchanged will form three equivalent bonds at 90° to one another. If quantization is changed, the three strongest bonds will lie at tetrahedral angles. But increase in the bond angle beyond the tetrahedral angle is not accompanied by a very pronounced decrease in bond strength. Thus three equivalent bond eigenfunctions in a plane, with maxima 120° apart, can be formed

$$\left.\begin{aligned}\psi_1 &= \frac{1}{\sqrt{3}}\,s + \sqrt{\frac{2}{3}}\,p_x \\ \psi_2 &= \frac{1}{\sqrt{3}}\,s - \frac{1}{\sqrt{6}}\,p_x + \frac{1}{\sqrt{2}}\,p_y \\ \psi_3 &= \frac{1}{\sqrt{3}}\,s - \frac{1}{\sqrt{6}}\,p_x - \frac{1}{\sqrt{2}}\,p_y\end{aligned}\right\} \qquad (10)$$

and these have a strength of 1.991, only a little less than that 2.000 of tetrahedral bonds (Fig. **6).** As a result, we may anticipate that in some cases the bond angles will be larger than 109°28′. The carbonate ion in calcite and the nitrate ion in sodium nitrate are assigned a plane configuration from the results of x-ray investigations. In these ions the oxygen atoms are only 2.25 Å. from one another, so that their characteristic repulsive forces must be large, resisting decrease in the bond angle (the smallest distance observed between oxygen ions in ionic crystals is *2.5* Å.). But repulsion of the oxygen atoms would not be very effective in increasing the bond angle in the neighborhood of 120°, so that we might expect equilibrium to be achieved'at a somewhat smaller angle, such as 118°. This would give $CO_3^=$ and NO_3^- a pyramidal structure, like that of NH_3. There would be two configurations possible for a given orientation of the O_3 plane, one in which the carbon (or nitrogen) atom was a short distance above this plane (taken as horizontal) and one with it below the plane. If there is appreciable interaction between these two, as there will be in case the pyramid is flat, the symmetric and antisymmetric combinations of the two will be the correct eigenfunctions, corresponding to the rapid inversion of the pyramid, with a frequency of the order of magnitude of the vibrational frequency of the complex ion along its symmetry axis. This inversion would introduce an effective symmetry plane normal to the three-fold axis, so that a pyramidal structure with rapid inversion is compatible with the x-ray observations.[26]

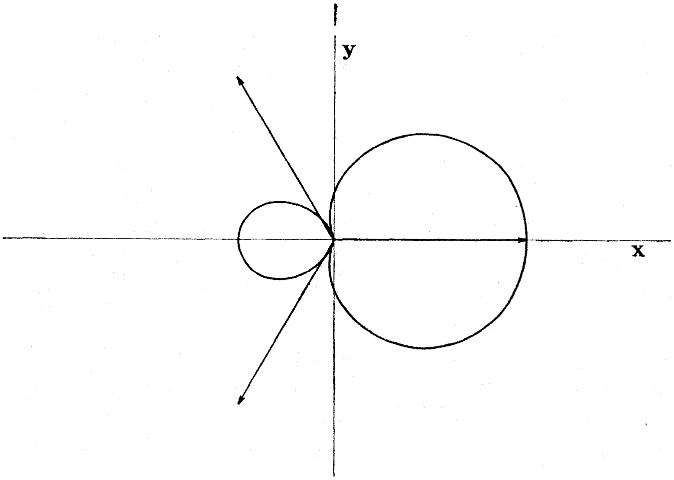

Fig. 6.—Polar graph of $\left|\frac{1}{\sqrt{3}} + \sqrt{2}\cos\varphi\right.$ in the xy plane, representing a trigonal eigenfunction. The maximum directions of the other two equivalent eigenfunctions are also shown.

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[26] Simulation of symmetry by molecules or complex ions in crystals has been discussed by Linus Pauling, Phys. *Rev., 36,* **430** (1930).

Thus the x-ray data do not decide between this structure and a truly plane structure. Evidence from another source is at hand, however. A plane $CO_3^=$ or NO_3^- ion should show three characteristic fundamental vibrational frequencies. These have been observed as reflection maxima in the infra-red region. But two of the maxima, at 7μ and 14μ, are double,[27] and this doubling, which is not explicable with a plane configuration, is just that required by a pyramidal structure, the separation of the components giving the frequency of inversion of the pyramid.[28]

In graphite each carbon atom is bound to three others in the same plane; and here the assumption of inversion of a puckered layer is improbable, because of the number of atoms involved. A probable structure is one in which each carbon atom forms two single bonds and one double bond with other atoms. These three bonds should lie in a plane, with angles 109°28′ and 125°16′, which are not far from 120°. Two single bonds and a double bond should be nearly as stable as four single bonds (in diamond), and the stability would be increased by the resonance terms arising from the shift of the double bond from one atom to another. But this problem and the closely related problem of the structure of aromatic nuclei demand a detailed discussion, perhaps along the lines indicated, before they can be considered to be solved.

The Structures of Simple **Molecules.**—The foregoing considerations throw some light on the structure of very simple molecules in the normal and lower excited states, but they do not permit such a complete and accurate discussion of these questions as for more complicated molecules, because of the difficulty of taking into consideration the effect of several unshared and sometimes unpaired electrons. Often the bond energy is not great enough to destroy s–p quantization, and the interaction between a bond and unshared electrons is more important than between a bond and other shared electrons because of the absence of the effect of concentration of the eigenfunctions.

Let us consider an atom forming a bond with another atom in the direction of the z axis. Then p_z and s form two eigenfunctions designated σ, p_x and p_y two designated π (one with a resultant moment of $+1$ along the z axis, one with -1). If s–p quantization is not broken, the strongest bond will be formed by p_z and weaker ones by π. If s–p quantization is broken, new eigenfunctions σ_b and σ_a will be formed from s and p_z. In this case the strongest bond is formed by the σ_b eigenfunction, which extends out toward the other atom, weaker ones are formed by π_+ and π_-, and an extremely weak one, if any, by σ_a. We can also predict the stability of

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[27] C. Schaefer, F. Matossi and F. Dane, *Z. Physik*, 45, **493** (1927).

[28] The normal states of these ions are similar to certain excited states of ammonia, which also show doubling. The frequency of inversion of the normal ammonia molecule is negligibly small.

unshared electrons; σ_o, involving s with its greater penetration of the atom core, will be more stable than **a.**

As examples we may discuss CO, CN, N_2 and NO. CO might be composed of normal or excited atoms, or even of ions. A neutral oxygen atom can form only two bonds. Hence a normal carbon atom, ^3P, which can also form two bonds, is at no disadvantage. We can write the following reaction, using symbols similar to those of Lennard-Jones[29] and Dunkel,[30] whose treatments of the electronic structure of simple molecules have several points of similarity with ours

$$\text{C } 2s^22p2p\ ^3P + \text{O } 2s^22p^22p2p\ ^3P \longrightarrow \text{CO } (2\sigma_o^2)(2\sigma_o^22\pi^2)\{2\sigma_b2\pi + 2\sigma_b2\pi\}^1\Sigma$$

$$:\text{C}. + \cdot\text{O}: \longrightarrow :\text{C}::\text{O}: \qquad \text{Normal state}$$

Here symbols in parentheses represent unshared electrons attached to C and **O**, respectively, and those in braces represent shared electrons. An excited carbon atom ^5S lies about 1.6 v. e. above the normal state, but can still form only a double bond with oxygen, so that the resultant molecule should be excited. We write

$$\text{C}^*\ 2s2p2p2p\ ^5S + \text{O } 2s^22p^22p2p\ ^3P \longrightarrow \text{CO}^*\ (2\sigma_o2\pi)(2\sigma_o^22\pi^2)\{2\sigma_b2\pi + 2\sigma_b2\pi\}\ ^3\Pi \text{ or } ^1\Pi$$

The resultant states are necessarily Π, for σ_b and one π are used for the bond, leaving on C a, and **a.** These two electrons may or may not pair with one another, giving $^1\Pi$ and $^3\Pi$, respectively. Of these $^3\Pi$ should be the more stable, for the two electrons are attached essentially to one atom, and the rules for atomic spectra should be valid. This is substantiated; the observed excited states $^3\Pi$ and $^1\Pi$ lie at 5.98 and 7.99 v. e., respectively. Another way of considering these three states is the following: to go from :C::O: to ·C::O: we lift an electron from the more deeply penetrating **a,** orbit to π; about 6–8 v. e. is needed for this, and the resultant state is either $^3\Pi$ or $^1\Pi$. This viewpoint does not necessitate the discussion of products of dissociation.

CN is closely similar. The normal nitrogen atom, $2s^22p2p2p\ ^4S$, can form three bonds, and more cannot be formed by an excited neutral atom (with five L electrons), so that there is no reason to expect excitation. But a normal carbon atom can form only a double bond, and an excited carbon atom, only 1.6 v. e. higher, can form a triple bond, which contributes about **3** v. e. more than a double bond to the bond energy. Hence we write

$$\text{C}^*\ 2s2p2p2p\ ^5S + \text{N } 2s^22p2p2p\ ^4S \longrightarrow \text{CN } (2\sigma_o)(2\sigma_o^2)\{2\sigma_b2\pi2\pi + 2\sigma_b2\pi2\pi\}^2\Sigma$$

$$.\text{C}. + \cdot\text{N}: \longrightarrow .\text{C}:::\text{N}: \qquad \text{Normal state}$$

The first excited state of the molecule, $:\text{C}::\underset{\cdot}{\text{N}}:$, is built from normal atoms, and has the term symbol $^2\Pi$. It lies 1.78 v. e. above the normal state.

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[29] J. E. Lennard-Jones, Trans. *Faraday Soc.*, 25, 668 (1929).

[30] M. Dunkel, *Z. physik. Chem.*, B7, 81 (1930).

Two normal nitrogen atoms form a normal molecule with a triple bond.

$$2\mathrm{N}\ 2s^2 2p 2p 2p\ {}^4S \longrightarrow \mathrm{N}_2(2\sigma_o{}^2)(2\sigma_o{}^2)\{2\sigma_b 2\pi 2\pi + 2\sigma_b 2\pi 2\pi\}\,{}^1\Sigma$$

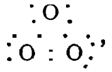
$$:\dot{\mathrm{N}}\cdot + \cdot\dot{\mathrm{N}}: \longrightarrow :\mathrm{N}:::\mathrm{N}: \qquad \textbf{Normalstate}$$

All other states lie much higher.

A normal oxygen atom and a normal nitrogen atom form a normal NO molecule with a double bond.

$$\mathrm{N}\ 2s^2 2p 2p 2p\ {}^4S + \mathrm{O}\ 2s^2 2p^2 2p 2p\ {}^3P \longrightarrow \mathrm{NO}(2\sigma_o{}^2 2\pi)(2\sigma_o{}^2 2\pi^2)\{2\sigma_b 2\pi + 2\sigma_b 2\pi\}\,{}^2\Pi$$

$$:\mathrm{N}. + \cdot\mathrm{O}: \longrightarrow :\underset{\cdot}{\mathrm{N}}::\underset{\cdot\cdot}{\mathrm{O}}: \qquad \textbf{Normal state}$$

This treatment sometimes fails for symmetrical molecules. Thus $:\ddot{\mathrm{O}}::\ddot{\mathrm{O}}:$ ${}^1\Sigma$ would be predicted for the normal state of O_2, whereas the observed normal state, ${}^3\Sigma$, lies 1.62 v. e. below this. It seems probable that the additional degeneracy arising from the identity of the two atoms gives rise to a new type of bond, the ***three-electron*** bond, and that in normal O_2 there are one single bond and two three-electron bonds, $:\mathrm{O}\overset{\cdots}{\underset{\cdots}{:}}\mathrm{O}:$, ${}^3\Sigma$; a definite decision regarding this question must await a detailed quantum-mechanical treatment. Evidence regarding the oxygen–oxygen single bond is provided by O_4, with the square structure $\begin{matrix} :\ddot{\mathrm{O}}:\ddot{\mathrm{O}}: \\ :\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}: \end{matrix}$. The 90° bond angles are expected, since quantization in s and p eigenfunctions is not changed. The equality in energy of O_4 and $2\mathrm{O}_2$ leads to an energy of 58,000 cal. per mole per single bond in O_4; the difference between this value and that for a carbon–carbon single bond (100,000 cal.) shows the greater bond-forming power of tetrahedral eigenfunctions over p eigenfunctions. Ozone, which very probably has the symmetrical arrangement , has 60° bond angles, and this distortion from the most favorable bond angle of 90° shows up in the bond energy, for the heat of formation of −34,000 cal. per mole leads to 47,000 cal. per mole per single bond, a decrease of 11,000 cal. over the favored O_4 bonds.

For some polyatomic molecules predictions can be made regarding the atomic arrangement from a knowledge of the electronic structure or ***vice versa.*** Thus $\cdot\mathrm{C}:::\mathrm{N}:$ ${}^2\Sigma$ can form a bond through the unpaired σ_o electron of carbon, and this bond will extend along the CN axis. Hence the molecules $\mathrm{H}:\mathrm{C}:::\mathrm{N}:$, $:\mathrm{N}:::\mathrm{C}:\mathrm{C}:::\mathrm{N}:$ and $:\ddot{\mathrm{Cl}}:\mathrm{C}:::\mathrm{N}:$ should be linear. This is verified by band spectral data.[31] The isocyanides, RNC, such as $\mathrm{H_3CNC}$, may be given either a triple or a double bond structure: $\mathrm{R}:\mathrm{N}:::\mathrm{C}:$ or $\mathrm{R}:\underset{\cdot\cdot}{\mathrm{N}}::\mathrm{C}:$. The first of these is built of the ions N^+ ${}^5S$ and C^- ${}^4S$, which may be an argument in favor of the second structure, built of normal

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[31] Private communication from Professor Richard M. Badger of this Laboratory, who has kindly provided me with much information concerning the results of band spectroscopy.

atoms.[32] A decision between the two alternatives could be made by determining the atomic arrangement of an isocyanide, for the triple bond gives a linear molecule, bond angle 180°, and the double bond a kinked molecule, bond angle between 90 and 109°28′.

The molecules and complex ions containing three kernels and sixteen L electrons form an interesting group. Of these CO_2, formed from excited carbon ${}^5S$ and normal oxygen atoms, would have the structure $:\ddot{O}::C::\ddot{O}:$. The two double bonds make the molecule linear, which is verified by both crystal structure and band spectral data. Crystal structure data also show N_2O to be linear, although it is not known whether or not the molecule has oxygen in the middle or at one end, as first suggested by Langmuir[33] and supported by the kernel-repulsion rule.[34] The known linear arrangement eliminates structures built of neutral atoms, $:N:O:N:$ and $:N::N:\ddot{O}:$, for these have bond angles between 90 and 125°. The structures $:\underset{\cdot\cdot}{N}::N::\underset{\cdot\cdot}{O}:$ and $:\underset{\cdot\cdot}{N}::O::\underset{\cdot\cdot}{N}:$, built from $N\ N^+\ O^-$ and $N^-\ O^{++}N^-$, respectively, would both be linear, and so compatible with the known arrangement. An *a priori* decision between them is difficult, although previously advanced arguments favor the unsymmetrical structure. Band spectra should soon decide the question.

The trinitride, cyanate, and isocyanate ions, the first two of which are known[35] to be linear, no doubt have identical electronic structures.

$$:\underset{\cdot}{\ddot{N}}\cdot^{-}\ {}^3P + \cdot\underset{\cdot}{\dot{N}}\cdot^{+}\ {}^5S + \cdot\underset{\cdot}{\ddot{N}}:^{-} \longrightarrow :\ddot{N}::N::\ddot{N}:^{-}$$

$$N^- + N^+ + N^- \longrightarrow N_3^- \text{ Trinitride ion}$$
$$N^- + C + O \longrightarrow NCO^- \text{ Cyanate ion}$$

The fulminate ion, CNO^-, probably has a structure intermediate between $:C::N::\ddot{O}:^-$ and $:C:::N:O:^-$; for since these two bond types have the same bond angles and term symbols (${}^1\Sigma$), they can form intermediate structures lying anywhere between the two extremes. Which extreme is the more closely approached could be determined from a study of the bond angles in un-ionized fulminate molecules, such as AgCNO or ONCHgCNO, for the first structure would lead to an angle of 125° between the CNO axis and the metal–carbon bond, the second to an angle of 180°.

Bonds Involving *d*-**Eigenfunctions**.—When d eigenfunctions as well as *s* and *p* can take part in bond formation, the number and variety of bonds which can be formed are increased. Thus with an s, a *p* and a d subgroup as many as nine bonds can be formed by an atom. It is found from a

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[32] Thus W. Heitler and G. Rumer, *Nachr. Ges. Wiss. Göttingen, Math. physik. Klasse*, 7, 277 (1930), in a paper on the quantum mechanics of polyatomic molecules, discuss only the second structure.

[33] I. Langmuir, THIS JOURNAL, **41**, 1543 (1919).

[34] Linus Pauling and S. B. Hendricks, *ibid.*, 48, 641 (1926).

[35] S. B. Hendricks and Linus Pauling, THIS JOURNAL, 47, 2904 (1925).

consideration of the eigenfunctions that all cannot be equivalent, but six equivalent bonds extending toward the corners of either a regular octahedron or a trigonal pyramid, four extending toward the corners of a tetrahedron or a square, etc., can be formed; and the strength and mutual orientation of the bonds are determined by the number of d eigenfunctions involved in their formation.

There are five d eigenfunctions in a subgroup with $l = 2$ and with given n. They are

$$\left.\begin{aligned} d_z &= \sqrt{5/4}\,(3\cos^2\theta - 1) \\ d_{y+z} &= \sqrt{15}\sin\theta\cos\theta\cos\varphi \\ d_{x+z} &= \sqrt{15}\sin\theta\cos\theta\sin\varphi \\ d_{x+,} &= \sqrt{15/4}\sin 2\theta\sin 2\varphi \\ d_x &= \sqrt{15/4}\sin^2\theta\cos 2\varphi \end{aligned}\right\} \qquad (11)$$

or any set of five orthogonal functions formed by linear combination of these. These functions are not well suited to bond formation. d_{y+z}, $d_{x+,}$ and d_{x+y}, which are similarly related to the x, y and z axes, respectively, have the form shown in Fig. 7. Each eigenfunction has maxima in four directions. d_x is similar in shape, differing from d_{x+y} only in a rotation of 45° about the z axis. d_z, shown in Fig. 8, has two maxima along the z axis, and a girdle about its waist.

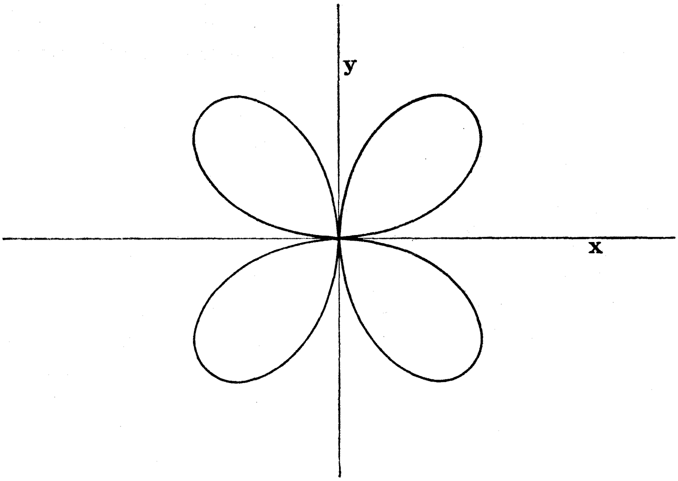

Fig. 7.—Polar graph of $\left|\frac{\sqrt{15}}{2}\sin^2\theta\sin 2\varphi\right.$ in the xy plane, representing the $d_x +$ eigenfunction.

Assuming as before that the dependence on r of the s, p and d eigenfunctions under discussion is not greatly different, the best bond eigenfunctions can be determined by the application of the treatment already applied to s and p alone, with the following results.

The best bond eigenfunction which can be obtained from s, p and d is

$$\frac{1}{3}s + \frac{1}{\sqrt{3}}p_z + \frac{\sqrt{5}}{3}d_z$$

and has a strength of 3. The best two equivalent bond eigenfunctions involving one d eigenfunction

$$\frac{1}{2\sqrt{3}}s + \frac{1}{\sqrt{2}}p_z + \frac{\sqrt{5}}{2\sqrt{3}}d_z \quad \text{and}$$
$$\frac{1}{2\sqrt{3}}s - \frac{1}{\sqrt{2}}p_z + \frac{\sqrt{5}}{2\sqrt{3}}d_z$$

are oppositely directed and have a strength of 2.96.

The atoms of the transition elements, for which d eigenfunctions need to be considered, are of such a size as usually to have a coordination number of 4 or 6, so that four or six equivalent bond eigenfunctions are here of especial interest. If there is available only one d eigenfunction to be combined with an s and three p eigenfunctions, then no more than five bond eigenfunctions can be formed. One may have the maximum strength 3, in which case the others are weak; or two may be strong and three weak; but *with a single d eigenfunction no more than four strong bonds can be formed, and these lie in a plane.* The fifth bond is necessarily weak. The four equivalent bond eigenfunctions formed from s, p and one d eigenfunction are

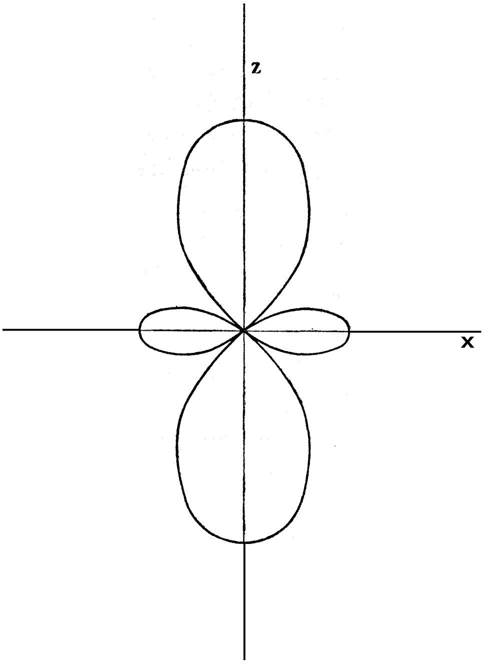

Fig. 8.—Polar graph of $\left|\frac{\sqrt{5}}{2}(3\cos^2\theta - 1)\right|$ in the xz plane, representing the d_z eigenfunction.

$$\left.\begin{aligned}
\psi_1 &= \frac{1}{2}s + \frac{1}{2}d_x + \frac{1}{\sqrt{2}}p_x \\
\psi_2 &= \frac{1}{2}s + \frac{1}{2}d_x - \frac{1}{\sqrt{2}}p_x \\
\psi_3 &= \frac{1}{2}s - \frac{1}{2}d_x + \frac{1}{\sqrt{2}}p_y \\
\psi_4 &= \frac{1}{2}s - \frac{1}{2}d_x - \frac{1}{\sqrt{2}}p_y
\end{aligned}\right\} \qquad (12)$$

One of these is shown in Fig. 9. These all have their maxima in the xy plane, directed toward the corners of a square. The strength of these bond eigenfunctions, 2.694, is much greater than that of the four tetrahedral eigenfunctions formed from s and p alone (2.00). But if three d eigenfunctions are available, stronger bonds directed toward tetrahedron corners can be formed. The equivalent tetrahedral bond eigenfunctions

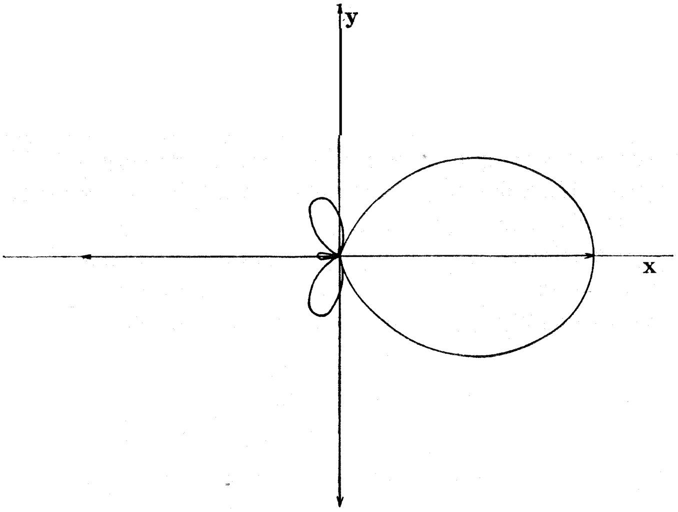

Fig. 9.—Polar graph of $\left| 1/2 + \sqrt{3/2}\cos\varphi + \frac{\sqrt{15}}{4}\cos 2\varphi \right|$ in the xy plane, representing one of the four equivalent dsp^2 bond eigenfunctions. The directions of the maxima of the four are represented by arrows.

$$\psi_{111} = \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(p_x + p_y + p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(d_{y+z} + d_{x+z} + d_{x+y})$$

$$\psi_{1\bar{1}\bar{1}} = \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(p_x - p_y - p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(d_{y+z} - d_{x+z} - d_{x+y})$$

$$\psi_{\bar{1}1\bar{1}} = \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(-p_x + p_y - p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(-d_{y+z} + d_{x+z} - d_{x+y})$$

$$\psi_{\bar{1}\bar{1}1} = \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(-p_x - p_y + p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(-d_{y+z} - d_{x+z} + d_{x+y})$$

have a strength of 2.950, nearly equal to the maximum **3.** These leave only two pure d eigenfunctions behind, however, the others being part d and part p. Thus we conclude that if there are three d eigenfunctions available, a transition group element forming four electron-pair bonds will direct them toward tetrahedron corners. Examples of such bonds are provided by $CrO_4^{=}$, $MoO_4^{=}$, etc. Only when one d eigenfunction alone is available will the four bonds lie in a plane. In compounds of bivalent nickel, palladium, and platinum, such as $K_2Ni(CN)_4$, $K_2Pd(CN)_4$, K_2PdCl_4, K_2PtCl_4, etc., there are eight unshared d electrons on each metal atom, which occupy four of the five d eigenfunctions. Hence the four added atoms or groups lie in a plane at the corners of a square about the metal atom. Such a configuration was assigned to palladous and platinous compounds by Werner because of the existence of apparent cis and *trans* compounds, and has been completely substantiated by the x-ray investigation of the chloropalladites and chloroplatinites.[36] The square configuration has not before been attributed to $K_2Ni(CN)_4$; it is supported by the observed isomorphism of the monoclinic crystals $K_2Pd(CN)_4 \cdot H_2O$ and $K_2Ni(CN)_4 \cdot H_2O$, and it will be shown in a following section that it is compatible with the magnetic data.

The non-existence of compounds K_3PtCl_5, etc., is explained by the weak bond-forming power (1.732) of the remaining eigenfunction p_z.

Now if two d eigenfunctions are available, six equivalent eigenfunctions

$$\left.\begin{aligned}
\psi_1 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{2}}\,p_z + \frac{1}{\sqrt{3}}\,d_z \\
\psi_2 &= \frac{1}{\sqrt{6}}\,s - \frac{1}{\sqrt{2}}\,p_z + \frac{1}{\sqrt{3}}\,d_z \\
\psi_3 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{12}}\,d_z + \frac{1}{2}\,d_x + \frac{1}{\sqrt{2}}\,p_x \\
\psi_4 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{12}}\,d_z + \frac{1}{2}\,d_x - \frac{1}{\sqrt{2}}\,p_x \\
\psi_5 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{12}}\,d_z - \frac{1}{2}\,d_x + \frac{1}{\sqrt{2}}\,p_y \\
\psi_6 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{12}}\,d_z - \frac{1}{2}\,d_x - \frac{1}{\sqrt{2}}\,p_y
\end{aligned}\right\} \qquad (13)$$

can be formed. These form strong bonds, of strength 2.923, directed toward the corners of a regular octahedron; and no stronger octahedral bonds can be formed even though more d eigenfunctions be available (Figs. 10 and 11). Hence we expect transition group atoms with six or less unshared electrons to form six electron-pair bonds. Examples of such compounds are numerous: $PtCl_6^{=}$, $Fe(CN)_6^{=}$, etc., although the definite assignment of an electron-pair bond structure rather than an ionic structure (as in $FeF_6^{\equiv}$, formed of Fe^{+++} and 6 F^-) can be made only after the discussion of paramagnetic susceptibility.

I have not succeeded in determining whether or not these octahedral eigenfunctions are the strongest six equivalent bond eigenfunctions which can be formed when more than two d's are available. The known structure of molybdenite, MoS_2, suggests that six bonds directed toward the corners of a trigonal prism are stable; but only a small increase in bond strength can possibly be obtained (from 2.923 to not over 3), and the mutual re-

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[36] R. G. Dickinson, This Journal, 44, 2404 (1922).

pulsion of the six atoms or groups will in most cases overcome this, if it does exist, and leave the octahedral configuration the stable one.

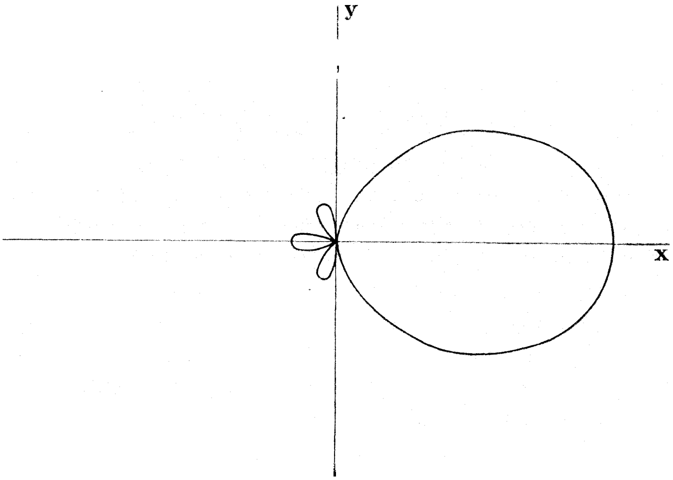

Fig. 10.—Polar graph of $|\psi_3|$ of Equation 13, in the *xy* plane, representing one of the six equivalent d^2sp^3 bond eigenfunctions (octahedral eigenfunctions).

II. The Magnetic Moments of Molecules and Complex Ions

The theory of the paramagnetic susceptibility of substances has been developed gradually over a long period of years through the efforts of a number of investigators. The theoretical calculation of the magnetic moments of complex molecules and ions has in particular attracted much attention recently, and both theoretical and empirical considerations have been used in developing rules applicable in various cases. The work reported in this paper provides little more than the justification and unification of previously developed rules. This finishing touch is, however, of much significance for the problem of the nature of the chemical bond; for it, in conjunction with the quantum mechanical discussion of the previous sections, permits definite conclusions to be drawn regarding type of bond in many molecules and complex ions from a knowledge of their magnetic moments, and conversely provides the basis for the definite prediction of magnetic moments from a knowledge of the type of bonds and the atomic arrangement.

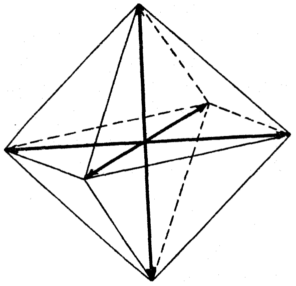

Fig. 11.—Diagram showing relative orientation in space of the directions of the maxima of the octahedral eigenfunctions.

The calculation of the magnetic moments of the rare-earth ions by

Hund[37] in 1926 and of oxygen and nitric oxide by Van Vleck[38] in 1928 were triumphs of the theory of spectra. The magnetic moment of an atom or monatomic ion with Russell–Saunders coupling of the quantum vectors is

$$\mu_J = g\sqrt{J(J+1)}$$

in which g, the Landé splitting factor, is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Here L, S, and J are the quantum numbers corresponding to the total orbital angular momentum of the electrons, the total spin angular momentum, and the resultant of these two. Hund predicted values of L, S, and J for the normal states of the rare-earth ions from spectroscopic rules, and calculated μ-values for them which are in generally excellent agreement with the experimental data for both aqueous solutions and solid salts.[39] In case that the interaction between L and S is small, so that the multiplet separation corresponding to various values of J is small compared with kT, Van Vleck's formula[38]

$$\mu_{LS} = \sqrt{4S(S+1) + J(J+1)}$$

is to be used.

But similar calculations for the iron-group ions show marked disagreement with experiment, and many attempts were made to explain the discrepancies. The explanation is simple: *in many condensed systems the perturbing effect of the atoms or molecules surrounding a magnetic atom destroys the contribution of the orbital momentum to the magnetic moment, which is produced entirely by the spin moments of unpaired electrons.*[40]

This conclusion is easily deduced from the consideration of the nature of eigenfunctions giving rise to magnetic moments. In an atom containing unpaired p electrons, say, a component of orbital magnetic moment of $\pm(h/2\pi)\cdot(e/2mc)$ is obtained when an unpaired electron is in a state given by the eigenfunction $p_x \pm i\,p_y$. Now if the perturbing influence of surrounding atoms or molecules is such as to make the perturbation energy for the eigenfunction p_x or p_y or any combination of them other than $p_x \pm i\,p_y$ greater than the field energy, this will be the correct zeroth order eigenfunction, and the atom will show no orbital magnetic moment. In an atom with Russell–Saunders coupling the interaction energy of L and S takes the place of the field energy, so that the criterion to be satisfied in order that the magnetic moment due to L be destroyed is that the perturbation energy due to surrounding atoms and ions be greater than the multiplet separation, which for the iron-group ions is of the order of magnitude of 1 v. e.[41]

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[37] F. Hund, *Z. Physik*, **33**, 345 (1925).

[38] J. H. Van Vleck, *Phys. Rev.*, 31, 587 (1928).

[39] The few discrepancies have been accounted for by S. Freed [THIS JOURNAL, 52, 2702 (1930)] and J. H. Van Vleck and A. Frank [*Phys. Rev.*, 34, 1494 (1929), and a paper delivered at the Cleveland meeting of the American Physical Society, December 31, 1930].

[40] This assumption was first made by E. C. Stoner, *Phil. Mag.*, 8, 250 (1929), in order to account for the observed moments of iron-group ions.

[41] Essentially the same conclusion has been announced by J. H. Van Vleck at the Cleveland meeting of the American Physical Society, December 31, 1930.

If the perturbation function shows cubic symmetry, and in certain other special cases, the first-order perturbation energy is not effective in destroying the orbital magnetic moment, for the eigenfunction p_x * i p_y leads to the same first-order perturbation terms as p_x or p_y or any other combinations of them. In such cases the higher order perturbation energies are to be compared with the multiplet separation in the above criterion.

In linear molecules only the component of orbital momentum normal to the figure axis is destroyed, that along the figure axis being retained. In non-linear molecules with strong interatomic interactions the concept of orbital angular momentum loses its significance.

The rare-earth ions owe their magnetic moments to an incompleted 4f subshell, which lies within an outer shell of 5*s* and 5*p* electrons, and is thus protected from strong perturbations by surrounding atoms. As a consequence the orbital magnetic moment is not destroyed, and the ion is not affected by its environment. But in the iron-group ions and other transition-group ions the incompleted subshell is the outermost one. Hence it is not surprising that the solvent molecules or the surrounding atoms or ions in a complex ion or a crystal interact sufficiently strongly with these atoms or ions to destroy, in whole, or in part, the orbital magnetic moment, leaving the spin moment, with perhaps a small contribution from the orbital moment in border-line cases. We can state with certainty that the formation of electron-pair bonds will destroy the orbital moment.

This greatly simplifies the theory of the magnetic moments of molecules and complex ions. *The magnetic moment of a molecule or complex ion is determined entirely by the number of unpaired electrons, being equal to*

$$\mu_S = 2\sqrt{S(S+1)}$$

in which S is one-half that number. The factor 2 is the g-factor for electron spin.

As a matter of fact, Sommerfeld[42] in 1924, a year before Hund's treatment of the rare-earth ions, noticed that the observed magnetic moments of K^+ and Ca^{++}, Ca^+ (spectroscopic), Ca (spectroscopic), Cr^{3+}, Cr^{++}, Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++} and Cu^+ are approximately reproduced by the above equation with $S = 0, {}^1/_2, 1, {}^3/_2, 2, {}^5/_2, 2, {}^3/_2, 1, {}^1/_2$ and 0, respectively. But with the development of spectral theory he apparently gave up this simple formula because of lack of a theoretical derivation of it, and it remained for Bose[43] in 1927 to state explicitly the assumption that only S contributes to the moment in these cases, without, however, explaining why L gives no contribution, and for Stoner[40] in 1929 to supply the explanation. The comparison of calculated and observed values is given in Table I. It may be pointed out that S increases to a maximum value of ${}^5/_2$ when the 3*d* subgroup is half filled; Pauli's principle requires that succeeding electrons decrease the spin, so that μ_S is symmetrical about

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[42] **A.** Sommerfeld, "Atombau," 4th ed., p. 639.

[43] D. M. Bose, *Z. Physik*, 43, 864 **(1927).**

this point. The agreement with experiment, while much better than for μ_J, is not perfect; ions with more than five $3d$ electrons are found to have moments larger than μ_S, while V^{3+} deviates in the other direction. Bose suggested that perhaps S could in some cases exceed the maximum value allowed by Pauli's principle, but the obviously correct explanation is that the perturbing effect of surrounding atoms is not sufficient completely to destroy the L moment. Hence the observed moment should lie between μ_S and μ_J, which it does in every case.

Since the interaction is not strong enough to destroy the L moment, we conclude that in aqueous solution and in some crystalline salts the atoms[44] Fe^{II}, Co^{III}, Co^{II}, Ni^{II} and Cu^{II} do not form strong electron-pair bonds with H_2O, Cl, or certain other atoms, the bonds instead being ion-dipole or ionic bonds.

The formation of a stable coordination compound involving the four tetrahedral sp^3 eigenfunctions might decrease the L contribution appreciably. It was indeed pointed out by Bose that in the compounds listed in the last column of Table II the observed moments approach more closely the theoretical values μ_S.

The Magnetic Moments of Complexes **with** Electron-Pair Bonds.—The peculiar magnetic behavior of some complex ions has attracted much attention. $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, for example, have $\mu = 2.0$ and 0.00, respectively, instead of the values 5.9 and 4.9 for Fe^{3+} and Fe^{++}. Welo and Baudisch[45] and later Sidgwick and Bose expressed essentially the following rule: the magnetic moment of a complex is the same as that of the atom with the same number of electrons as the central atom of the complex, counting two for each electron-pair bond. Fe^{++} has 24 electrons; adding 12 for the six bonds gives **36,** the electron number of krypton, so that the diamagnetism of the ferrocyanide ion is explained. This rule is satisfactory in many cases,. but there are also many exceptions. Thus $[Ni(CN)_4]^=$ is diamagnetic, although the above rule would make it as paramagnetic as $[Ni(NH_3)_4]^{++}$.

The whole question is clarified when considered in relation to the foregoing quantum mechanical treatment of the electron-pair bond. For the iron-group elements the following rules follow directly from that treatment and from the rules of line spectroscopy.

1. Bond eigenfunctions for iron-group atoms are formed from the nine eigenfunctions $3d^6$*, 4s and* $4p^3$*, as described in preceding sections. One bond eigenfunction is needed for each electron-pair bond.*

2. The remaining (unshared) electrons are to be introduced into the 3d eigenfunctions not involved in bond formation.

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[44] The symbol Fe^{II} is used for bivalent iron, etc., when the type of bond is undetermined.

[45] L. A. Welo and O. Baudisch, *Nature*, 116, 606 (1925).

TABLE II

MAGNETIC MOMENTS OF IRON-GROUP IONS[a]

Ion	Normal state	μ_J	μ_S	Obs. moment in aqueous soln.	Solid salts, probable coördination number 6		Solid salts, coördination number	
K^+, Ca^{++}, Sc^{3+}, Ti^{4+}	$^1S_0$	0.00	0.00	0.00				
V^{4+}	$^2D_{3/2}$	1.55	1.73	1.7				
V^{3+}	$^3F_2$	1.63	2.83	2.4				
V^{++}, Cr^{3+}	$^4F_{3/2}$	0.78	3.88	3.8–3.9	$Cr_2O_3 \cdot 7H_2O$	3.85		
					$CrCl_3$	3.81		
Cr^{++}, Mn^{3+}	$^5D_0$	0.00	4.90	4.8–4.9				
Mn^{++}, Fe^{3+}	$^6S_{5/2}$	5.91	5.91	5.8	$MnCl_2$	5.75		
					$MnSO_4$	5.87		
					$MnSO_4 \cdot 4H_2O$	5.87		
					$Fe_2(SO_4)_3$	5.86		
					$(NH_4)_2Fe_2(SO_4)_4$	5.86		
Fe^{++}, Co^{3+}	$^5D_4$	6.76	4.90	5.3	$FeCl_2$	5.23	$Fe(N_2H_4)_2Cl_2$	4.87
					$FeCl_2 \cdot 4H_2O$	5.25		
					$FeSO_4$	5.26		
					$FeSO_4 \cdot 7H_2O$	5.25		
					$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	5.25		
Co^{++}	$^4F_{9/2}$	6.68	3.88	5.0–5.2	$CoCl_2$	5.04	$Co(N_2H_4)_2SO_3 \cdot H_2O$	4.31
					$CoSO_4$	5.04–5.25	$Co(N_2H_4)_2(CH_3COO)_2$	4.56
					$CoSO_4.7H_2O$	5.06	$Co(N_2H_4)_2Cl_2$	4.93
					$(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$	5.00		
Ni^{++}	$^3F_4$	5.64	2.83	3.2	$NiCl_2$	3.24–3.42	$Ni(N_2H_4)_2SO_3$	3.20
					$NiSO_4$	3.42	$Ni(N_2H_4)_2(NO_2)_2$	2.80
							$Ni(NH_3)_4SO_4$	2.63
							$Ni(C_2H_4(NH_2)_2)_2(SCN)_2H_2O$	2.63
Cu^{++}	$^2D_{5/2}$	3.56	1.73	1.9–2.0	$CuCl_2$	2.02	$Cu(NH_3)_4(NO_3)_2''$	1.82
					$CuSO_4$	2.01	$Cu(NH_3)_4SO_4 \cdot H_2O$	1.81
Cu^+, Zn^{++}	$^1S_0$	0.00	0.00	0.00				

[a] Observed magnetic moments, other than those in the last column, are from "International Critical Tables."

3. The normal state is the state with the *maximum* resultant spin S allowed by *Pauli's* principle.

These rules apply also to the palladium and platinum groups, the eigenfunctions involved being $4d^5 5s5p^3$ and $5d^5 6s6p^3$, respectively.

There are several important types of molecules and complexes to be given separate discussion.

If the bonds are ionic or ion-dipole bonds, the magnetic moments are those of the isolated central ions, given in the first column of moments in Table III. If the complex involves electron-pair bonds formed from sp^3 alone, such as four tetrahedral sp^3 bonds, the magnetic moments are the same, for the five d eigenfunctions are still available for the remaining electrons. The hydrazine and ammonia complexes mentioned above come in this class.

If four strong bonds involving a d eigenfunction are formed (giving a square configuration), only four d eigenfunctions are available for the additional electrons. The magnetic moments are then those given in the second column of the table. Examples of such compounds are $K_2Ni(CN)_4$, $K_2Pd(CN)_4 \cdot H_2O$, K_2PdCl_4, K_2PtCl_4, $K_2Pt(C_2O_4)_2 \cdot 2H_2O$ and $Pt(NH_3)_4SO_4$. With eight unshared d electrons, these should all be diamagnetic. This has been experimentally verified for the first and the last three compounds; data for the others are not available. The square configuration has been experimentally verified for the chloropalladites and chloroplatinites, as mentioned before. It can be predicted that in the $[Pt(C_2O_4)_2 \cdot 2H_2O]^=$ complex the two oxalate groups lie in a plane, each attached to the platinum atom by two electron-pair bonds of the type dsp^2. The two water molecules, if attached to the complex, are held by ion-dipole bonds.

In complexes in which the central atom forms a coördinated octahedron of six atoms or groups, the bonds may be any of several types. If they are all ionic or ion-dipole bonds, the moments are those in the first column. If four electron-pair bonds are formed, these must be dsp^2 and lie in a plane (sp^3 gives tetrahedral bonds); the $[Pt(C_2O_4)_2 \cdot 2H_2O]^=$ ion is of this type, assuming that the water molecules are part of the complex. The moments are then those of the second column. If six electron-pair bonds are formed, only three d eigenfunctions are left for the additional electrons, giving the magnetic moments of the third column. It is seen that in atoms with three or fewer unshared electrons magnetic data provide no information as to bond type with coordination number six, but that in other cases a definite statement can be made as to the type of bond when magnetic data are available. The observed magnetic moments are collected in Table IV. From them we deduce that trivalent and bivalent manganese, chromium, iron, and cobalt form six strong electron-pair bonds with cyanide groups, and in some cases with other groups, including NH_3, Cl and NO_2.[46] Tri-

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[46] An electron-pair bond with a water molecule may perhaps be formed when induced by other strong bond-forming groups in the complex.

TABLE III

PREDICTED MAGNETIC MOMENTS OF COMPLEXES CONTAINING TRANSITION ELEMENTS

			For ion or $4sp^3$ bonds	For 4 dsp^2 bonds	For 6 d^2sp^3 bonds	For 8 d^4sp^3 bonds
$\mathrm{K^{I}}$ $\mathrm{Ca^{II}}$ $\mathrm{Sc^{III}}$ $\mathrm{Ti^{IV}}$, etc.	$\mathrm{Rb^{I}}$ $\mathrm{Sr^{II}}$ $\mathrm{Y^{III}}$ $\mathrm{Zr^{IV}}$ $\mathrm{Nb^{V}}$ $\mathrm{Mo^{VI}}$	$\mathrm{Cs^{I}}$ $\mathrm{Ba^{II}}$—$\mathrm{Hf^{IV}}$$\mathrm{Ta^{V}}$ $\mathrm{W^{VI}}$	0.00	0.00	0.00	0.00
$\mathrm{V^{IV}}$	$\mathrm{Nb^{IV}}$$\mathrm{Mo^{V}}$	$\mathrm{W^{V}}$	1.73	1.73	1.73	1.73
$\mathrm{V^{III}}$ $\mathrm{Cr^{IV}}$	$\mathrm{Mo^{IV}}$ $\mathrm{Ru^{VI}}$	$\mathrm{W^{IV}}$ $\mathrm{Os^{VI}}$	2.83	2.83	2.83	0.00
$\mathrm{V^{II}}$ $\mathrm{Cr^{III}}$ $\mathrm{Mn^{IV}}$	$\mathrm{Mo^{III}}$		3.88	3.88	3.88	
$\mathrm{Cr^{II}}$ $\mathrm{Mn^{III}}$ $\mathrm{Fe^{IV}}$	$\mathrm{Mo^{II}}$ $\mathrm{Ru^{IV}}$	$\mathrm{Os^{IV}}$	4.90	4.90	2.83	
$\mathrm{Mn^{II}}$ $\mathrm{Fe^{III}}$ $\mathrm{Co^{IV}}$	$\mathrm{Ru^{III}}$	$\mathrm{Os^{III}}$ $\mathrm{Ir^{IV}}$	5.91	3.88	1.73	
$\mathrm{Fe^{II}}$ $\mathrm{Co^{III}}$	$\mathrm{Ru^{II}}$$\mathrm{Rh^{III}}$$\mathrm{Pd^{IV}}$	$\mathrm{Ir^{III}}$ $\mathrm{Pt^{IV}}$	4.90	2.83	0.00	
$\mathrm{Co^{II}}$ $\mathrm{Ni^{III}}$	$\mathrm{Rh^{II}}$		3.88	1.73		
$\mathrm{Ni^{II}}$	$\mathrm{Rh^{I}}$ $\mathrm{Pd^{II}}$ $\mathrm{Ag^{III}}$	$\mathrm{Pt^{II}}$ $\mathrm{Au^{III}}$	2.83	0.00		
$\mathrm{Cu^{II}}$			1.73			
$\mathrm{Cu^{I}}$ $\mathrm{Zn^{II}}$ $\mathrm{Ca^{III}}$ $\mathrm{Ge^{IV}}$, etc.	$\mathrm{Ag^{I}}$ $\mathrm{Cd^{II}}$ $\mathrm{In^{III}}$ $\mathrm{Sn^{IV}}$ $\mathrm{Sb^{V}}$ $\mathrm{Te^{VI}}$	$\mathrm{Au^{I}}$ $\mathrm{Hg^{II}}$ $\mathrm{Tl^{III}}$ $\mathrm{Pb^{IV}}$ $\mathrm{Bi^{V}}$ $\mathrm{Po^{VI}}$	0.00			

valent iron apparently does not form electron-pair bonds with fluorine (in $[FeF_5 \cdot H_2O]^-$); although investigation of $(NH_4)_3FeF_6$ is to be desired in order to be sure of this conclusion. Ir^{III} and Pt^{IV} form six electron-pair bonds with Cl, NO_2 or NH_3.

TABLE IV

OBSERVED MAGNETIC MOMENTS OF COMPLEXES CONTAINING TRANSITION ELEMENTS[a]

	μ		μ
$K_3[Mn(CN)_6]$	3.01	$[Co(NH_3)_6]Cl_3$	0.00
$K_4[Cr(CN)_6]$	3.3	$[Co(NH_3)_5Cl]Cl_2$	.00
$K_3[Fe(CN)_6]$	2.0	$[Co(NH_3)_4Cl_2]Cl$	.00
$K_4[Mn(CN)_6]$	2.0	$[Co(NH_3)_3(NO_2)_3]$	.00
$K_4[Fe(CN)_6] \cdot 3H_2O$	0.00	$[Co(NH_3)_5H_2O]_2(C_2O_4)_3$	.00
$Na_3[Fe(CN)_5NH_3]$	.00		
$K_3[Co(CN)_6]$	.00	$K_2Ni(CN)_4$	0.00
$(NH_4)_2[FeF_5 \cdot H_2O]$	5.97	$K_2Ni(CN)_4 \cdot H_2O$	.00
$K_4[Mo(CN)_8]$	0.00	K_2PtCl_4	.00
$K_4[W(CN)_8] \cdot 2H_2O$	.00	$K_2Pt(C_2O_4)_2 \cdot 2H_2O$	.00
$Na_3[IrCl_2(NO_2)_4]$	.00	$Pt(NH_3)_4SO_4$	.00
$[Ir(NH_3)_5NO_2]Cl_2$	.00		
$[Ir(NH_3)_4(NO_2)_2]Cl$	.00	$Na_2[Fe(CN)_5NO] \cdot 2H_2O$	.00
$[Ir(NH_3)_3(NO_2)_3]$	.00	$[Ru(NH_3)_4 \cdot NO \cdot H_2O]Cl_3$	.00
$K_2[PtCl_6]$	.00	$[Ru(NH_3)_4 \cdot NO \cdot Cl]Br_2$	.00
$[Pt(NH_3)_6]Cl_4$	.00	$[Co(NH_3)_5NO]Cl_2$	2.81
$[Pt(NH_3)_5Cl]Cl_3$	.00		
$[Pt(NH_3)_4Cl_2]Cl_2$	.00	$Ni(CO)_4$	0.00
$[Pt(NH_3)_3Cl_3]Cl$	.00	$Fe(CO)_5$	.00
$[Pt(NH_3)_2Cl_4]$	.00	$Cr(CO)_6$	.00

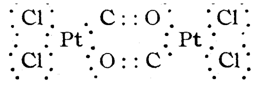
[a] Values quoted are from "International Critical Tables" or from W. **Biltz**, *Z. anorg. Chem.*, 170, 161 (1928), and D. M. Bose, *Z. Physik*, 65, 677 (1930). I am indebted to Mr. P. D. Brass for collecting from the literature some of the data in this table.

The moments of complexes containing NO offer a puzzling problem. The diamagnetism of compounds of iron and ruthenium suggests that Fe^{IV} and Ru^{IV} form a double bond with NO, making seven bonds in all, which woud lead to $\mu = 0$. But this structure cannot be applied to $[Co(NH_3)_5NO]Cl_2$, which has a moment corresponding to a triplet state. Further study of such complexes is needed.

The observed diamagnetism of the ions $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$ shows that the central atom forms eight electron-pair bonds, involving the eigenfunctions d^4sp^3 (fourth column of Table III).

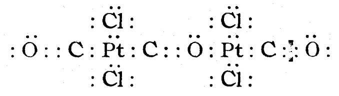
The metal carbonyls $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ are observed to be diamagnetic. This follows from the theoretical discussion if it is assumed that an electron-pair bond is formed with each carbonyl; for the nine eigenfunctions available ($3d^54s4p^3$) are completely filled by the n bonds and $2(9-n)$ additional electrons attached to the metal atom ($n = 4, 5, 6$). The theory also explains the observed composition of these unusual substances; for the formulas $M(CO)_n$, with n = 4, 5, and 6, respectively, follow at once from the assumption that CO molecules add on as long as bond eigenfunctions are available. Since a single unshared electron can occupy an eigenfunction, this assumption leads to the formula $Co(CO)_4$, which is known to be correct. This substance should have $\mu = 1.73$. The compounds $Mn(CO)_5$ and $V(CO)_6$ should also exist, and have $\mu = 1.73$. $Co(CO)_4$ and $Mn(CO)_5$ should form un-ionized diamagnetic cyanides, $[Co(CO)_4CN]$ and $[Mn(CO)_5CN]$, while $V(CO)_6$ would not form a stable cyanide, since steric effects would prevent the cyanide group from forming an electron-pair bond with the vanadium atom, and ionic cyanides are formed only by strong metals. It is interesting to note the effect of the four strong bond eigenfunctions and one weak one formed from dsp^3; whereas nickel forms no lower carbonyl than $Ni(CO)_4$, iron forms $Fe(CO)_4$ and $Fe_2(CO)_9$ in addition to $Fe(CO)_5$.

The palladium and platinum metals also form carbonyl compounds. Of the expected compounds $Pd(CO)_4$, $Pt(CO)_4$, $Ru(CO)_5$, $Os(CO)_5$, $Mo(CO)_6$, and $W(CO)_6$ only $Mo(CO)_6$ has been prepared, although some unsaturated ruthenium carbonyls have been prepared. The compounds $Pd(CO)_2Cl_2$, $Pt(CO)_2Cl_2$, $K[PtCOCl_3]$, etc., show the stability of the four dsp^2 bonds. It would be interesting to determine whether or not each CO is bonded to two metal atoms in compounds such as $[Pt(CO)Cl_2]_2$, whose structure is predicted to be



$$\begin{array}{ccccc} \vdots Cl \vdots & & .C::O\dot{} & & \vdots Cl \vdots \\ & \vdots Pt \vdots & & \vdots Pt \vdots & \\ \vdots Cl \vdots & & \dot{}O::C. & & \vdots Cl \vdots \end{array}$$

with the whole molecule in one plane. The compounds $2PdCl_2{\cdot}3CO$ and $2PtCl_2{\cdot}3CO$ probably have the structure



$$\begin{array}{c} :\ddot{Cl}: \qquad :\ddot{Cl}: \\ :\ddot{O}::C:\ddot{Pt}:C::\ddot{O}:\ddot{Pt}:C::\ddot{O}: \\ :\ddot{Cl}: \qquad :\ddot{Cl}: \end{array}$$

or one of the structures isomeric with this.

This by no means exhaustive discussion may serve to indicate the value of the information provided by magnetic data relative to the nature of the chemical bond. The quantum-mechanical rules for electron-pair bonds are essential to the treatment. Much further information is provided when these methods of attack are combined with crystal structure data, a topic which has been almost completely neglected in this paper. It has been found that the rules for electron-pair bonds permit the formulation of a set of structural principles for non-ionic inorganic crystals similar to that for complex ionic crystals; the statement of these principles and applications illustrating their use will be the subject of an article to be published in the *Zeitschrift für Kristallographie.*

Summary

With the aid of the quantum mechanics there is formulated a set of rules regarding electron-pair bonds, dealing particularly with the strength of bonds in relation to the nature of the single-electron eigenfunctions involved. It is shown that one single-electron eigenfunction on each of two atoms determines essentially the nature of the electron-pair bond formed between them; this effect is accentuated by the phenomenon of concentration of the bond eigenfunctions.

The type of bond formed by an atom is dependent on the ratio of bond energy to energy of penetration of the core (*s*–*p* separation). When this ratio is small, the bond eigenfunctions are *p* eigenfunctions, giving rise to bonds at right angles to one another; but when it is large, new eigenfunctions especially adapted to bond formation can be constructed. From *s* and *p* eigenfunctions the best bond eigenfunctions which can be made are four equivalent tetrahedral eigenfunctions, giving bonds directed toward the corners of a regular tetrahedron. These account for the chemist's tetrahedral atom, and lead directly to free rotation about a single bond but not about a double bond and to other tetrahedral properties. A single *d* eigenfunction with *s* and *p* gives rise to four strong bonds lying in a plane and directed toward the corners of a square. These are formed by bivalent nickel, palladium, and platinum. Two *d* eigenfunctions with *s* and *p* give six octahedral eigenfunctions, occurring in many complexes formed by transition-group elements.

It is then shown that (excepting the rare-earth ions) the magnetic moment of a non-linear molecule or complex ion is determined by the number of unpaired electrons, being equal to $\mu_S = 2\sqrt{S(S+1)}$, in which S is half that number. This makes it possible to determine from magnetic data which eigenfunctions are involved in bond formation, and so to decide between electron-pair bonds and ionic or ion-dipole bonds for various complexes. It is found that the transition-group elements almost without exception form electron-pair bonds with CN, ionic bonds with F, and ion-dipole bonds with H_2O; with other groups the bond type varies.

Examples of deductions regarding atomic arrangement, bond angles and other properties of molecules and complex ions from magnetic data, with the aid of calculations involving bond eigenfunctions, are given.

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NOTES

A Method of Sealing Substances in Ampullae with Inert Gases.—Usually substances susceptible to oxidation can be sealed in the vacuum of the mercury pump. However, some substances (e. g., samples of vitamin-bearing extracts and the like) cannot thus be sealed, due to voluminous foaming, sputtering, etc. In such cases, the substances must be sealed in with an inert gas. There are several methods (and ampullae with two tubulures) which permit of this. The author uses a method which is almost self-explanatory from the accompanying figure, and among several other advantages permits the use of the ordinary routine ampullae with a single tubulure.

A short piece of rubber tubing is attached to the tubulure. The other end of this tubing is stoppered with a piece of glass rod, and (at A) is provided with a 1-cm. lengthwise slit, *i.* e., a Bunsen valve. In the figure, B represents a hollow pointed surgical needle, of adequate length and lumen. The needle is passed through one wall of the tubing, and is pushed down into the ampulla almost to the surface of the substance. An inert gas (carbon dioxide or nitrogen) is conducted into the needle through tubing C, until all the air in the ampulla has been displaced and driven out through slit A. At this point the source of the inert gas is shut off, and the needle is then drawn up until its point is on a level with D. The ampulla is thereupon sealed by fusing off at E. The arrangement of Bunsen valve and needle can be used repeatedly. Due to the fact that the point of the needle can be raised or lowered, it can be adjusted to approach the surface of the substance, no matter whether large or small amounts are being sealed up. This will frequently be found to be advantageous.

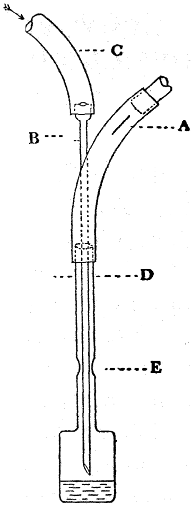

Fig. 1.

ZURICH, SWITZERLAND ALBERT B. WEINHAGEN

RECEIVED DECEMBER 22, 1930
PUBLISHED APRIL 6, 1931

Preparation of Starch Solution for Use in Iodimetric Titrations.—Some years ago the writers and John Field, 2d [THIS JOURNAL 48, 1299 (1926)] pointed out that clear starch solutions showing little or no Tyndall effect could be obtained for iodimetric titrations by leaching dry starch that had been ground for a long time in a pebble mill. The writers have found that equally satisfactory solutions may be obtained by leaching the well-known breakfast food, puffed rice. The tedious grinding in the pebble mill can thus be avoided.

FROM THE FOOD RESEARCH INSTITUTE AND THE
DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIFORNIA
C. L. ALSBERG
E. P. GRIFFING

RECEIVED FEBRUARY 25, 1931
PUBLISHED APRIL 6, 1931

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE RATE OF HYDROGENATION OF ACETOACETIC ESTER, DEHYDROACETIC ACID, BENZENE, PHENOL AND ANILINE OVER NICKEL AT PRESSURES FROM 27 TO 350 ATMOSPHERES

BY HOMER ADKINS, HOWARD I. CRAMER AND RALPH CONNOR

RECEIVED JULY 28, 1930 PUBLISHED APRIL 6, 1931

There appears to be comparatively little information available as to the relation of the pressure of hydrogen to the rate of hydrogenation of liquids with nickel catalysts. Ipatiev believed that pressures of the order of a hundred atmospheres were advantageous, while others have been but little impressed by the advantages of such pressures.[1] The experimental work described in this paper was performed in order to find out, in the case of a few supposedly representative compounds, what pressures could most advantageously be used for their hydrogenation.

The disadvantages in the use of pressures above a few atmospheres are obvious. Glass apparatus and rubber tubing may not be used, so that the assistance of a mechanic and materials often not available in the laboratory are required for the construction of the apparatus. The advantages in the use of pressures up to 80 or 150 atmospheres are no less real. Pressures of these magnitudes raise the boiling points of all organic materials which are liquids under laboratory conditions to 190° or above. This makes it possible to use any of the common solvents and to subject in the liquid phase almost all organic compounds to the action of hydrogen and the nickel catalyst. It also makes it possible to store in the reduction chamber a much greater quantity of hydrogen and thus avoid any auxiliary tank such as is necessary in reduction of pressures of a few atmospheres. This makes it possible to use a very simple set-up which includes only one inexpensive valve of the type designed for holding pressure on but one side. (Such an apparatus is manufactured by the Burgess–Parr Co. of Moline, Ill.) At least for small-scale operation in the laboratory the advantages of using pressures in the range 60 to 120 or 150 atmospheres as compared with pressures below perhaps 5 atmospheres seem to be

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[1] *Sabatier and Reid, "Catalysis in Organic Chemistry,"* D. *Van* Nostrand Co., New *York*, 1922, p. *207.*

quite considerable with no material increase in danger, inconvenience or expense. The use of pressures materially higher than these necessitates additional and more expensive equipment, for hydrogen is usually purchased in tanks holding the gas under a pressure of about 125 atmospheres, A bomb filled at this pressure and heated to 200°, which may be regarded as a reasonable upper limit necessary for operation with a nickel catalyst, would show a pressure of about 190 atmospheres. This represents then the maximum pressure which may be obtained without considerable additional equipment.

Acetoacetic ester, dehydroacetic acid, benzene, aniline and phenol were selected as representative compounds for testing out the practical advantages of various pressures up to 350 atmospheres. Acetoacetic ester and benzene absorbed one mole and three moles of hydrogen, respectively, while phenol and aniline were not completely reduced under the conditions selected, the ratio of catalyst to reactant and the temperature being too low for complete reduction. These compounds were completely reduced if a higher ratio of catalyst or temperature was used. In so far as our experience goes dehydroacetic acid requires a second or third application of catalyst in order to obtain complete reduction. "Complete reduction" in the two lower ranges of pressure means three moles of hydro-

TABLE I

THE RATE OF REDUCTION OF ACETOACETIC ESTER, BENZENE, PHENOL AND ANILINE AT VARIOUS PRESSURES

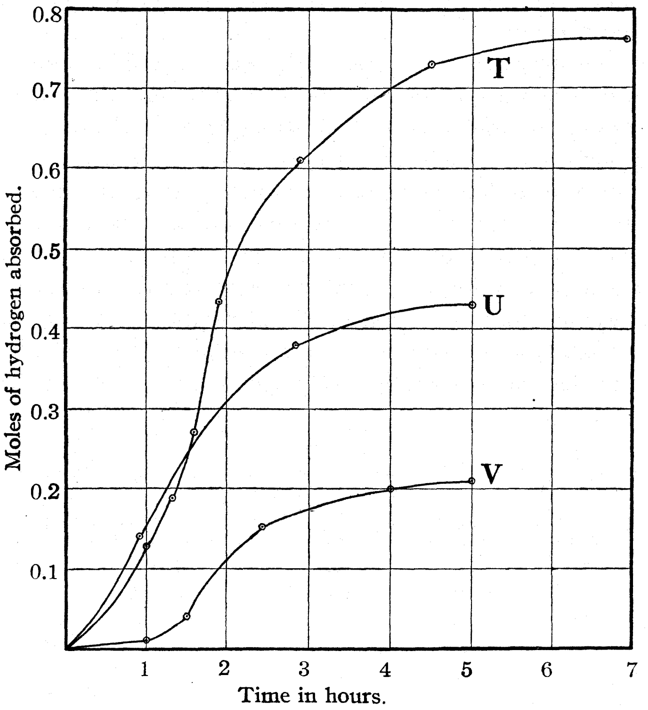
Time,	% of acetoacetic ester hydrogenated (a)			% of benzene hydrogenated (b)		
hrs.	27 ± 13 atm.	122 t 13 atm.	3.50 ± 6 atm.	30 ± 17 atm.	169 ± 19 atm.	323 ± 17 atm
0	21	36	83	17	29	34
0.5	40	62	100	40	68	75
1.0	55	76		61	90	93
1.5	72	85		76	98	100
2.0	86	91		87	100	
2.5		95		96		
3.0	97	98		100		

Time.	% of aniline hydrogenated (c)			% of phenol hydrogenated (d)		
hrs.	34 ± 14 atm.	190 ± 20 atm.	340 ± 15 atm.	40 ± 20 atm.	150 ± 26 atm.	330 ± 15 atm
0	4	17	15	5	13	20
1	9	34	36	27	49	49
2	13	44	49	41	63	62
3	17	51	59	50	73	70
4	21	56	64	59	81	
5	25	62	70	67	85	
6	29	65	75	72	87	
7	32	68		76		

(a) 0.39 mole of acetoacetic ester with 2 g. of catalyst at 150°. (b) 0.16 mole of benzene with 1 g. of catalyst at 120°. (c) 0.33 mole of aniline in 50 ml. of methyl cyclohexane with 2 g. of catalyst at 175°. (d) 0.33 mole of phenol with 1 g. of catalyst at 120°.

gen per mole of dehydroacetic acid, while at the higher pressure it means five moles of hydrogen per mole of acid. The products formed in the hydrogenation of acetoacetic ester and dehydroacetic acid have been considered in an earlier paper.[2]

There is shown in Fig. 1 the effect of increased pressure upon the rate and extent of absorption of hydrogen by dehydroacetic acid. The data given in Table I show the rate of progress toward complete reduction at different pressures for acetoacetic ester, benzene, phenol and aniline. Zero time was taken as the time at which the thermocouple in the bomb first showed the temperature which had been selected for allowing the reaction to proceed. The figures given in the tables are for individual experiments which have been duplicated at least once. The general effects have been observed in numerous experiments. The duplicate experiments showed



T, 323 atm.; U, 149 atm.; V, 108 atm.

Fig. 1.—The rate of absorption of hydrogen by dehydroacetic acid at various pressures. The moles of hydrogen absorbed at three pressures are plotted against the time in hours for the reduction of 50 g. (0.3 mole) of dehydroacetic acid in 100 ml. of methylcyclohexane, using 4 g. of a nickel catalyst at 185–190°.

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[2] Adkins, Connor and Cramer, THIS JOURNAL, 52, 5192 (1930).

no variation greater than 3% from the values reported in the tables. The experimental methods, catalysts, etc., were those described in a recent paper.[3] It must be pointed out that in measuring the rate of reduction, the absorption of hydrogen at a given time must necessarily be calculated from measurements of pressure at the temperature of reduction. This presents no particular difficulties in measuring the rate of reduction of compounds which are quantitatively reduced under the experimental conditions, for the final drop in pressure at the temperature of reduction represents 100% reduction and the percentage reduction at various times may be simply and accurately calculated. If the compound under consideration is not completely reduced, then the drop in pressure must be evaluated in terms of the standardization figures for the apparatus determined for some other compound such as acetone which is quantitatively reduced. At the higher pressures and temperatures the results so obtained are less accurate than at lower pressure.

Summary

The relationship of pressure to the rate of catalysis by nickel of the hydrogenation of acetoacetic ester, dehydroacetic acid, benzene, phenol and aniline has been found to differ greatly among these five compounds. It was entirely feasible to reduce acetoacetic ester at pressures in the vicinity of 30 atmospheres but the rate of reduction was greatly increased by increases in pressure, especially in the range from 120 to 350 atmospheres. Dehydroacetic acid reduced more than twice as rapidly at 149 as at 108 atmospheres and about four times as rapidly at 323 as at 108 atmospheres. It was found impractical to reduce aniline in the 30 atmosphere range. Increasing the pressure greatly increased the rate of hydrogenation, but increasing the pressure in the higher ranges up to 350 atmospheres was not found to be particularly advantageous. The rate of reduction of phenol and of benzene proceeded well in the 30 to 40 atmosphere range, increased with pressure to the 150 to 170 atmosphere range but was not sensitive to further increase in pressure up to 330 atmospheres.

MADISON, WISCONSIN

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[3] Adkins and Cramer, THIS JOURNAL, 52,4349 (1930).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

REDUCTION OF NITROSOPHENOL BY IRON AND HYDROCHLORIC ACID

BY KONOMU MATSUMURA AND CHUSABURO SONE

RECEIVED AUGUST 1, 1930 PUBLISHED APRIL 6, 1931

In a study of quinoline syntheses, 7-amino-5-acetyl-8-hydroxyquinoline was desired. On treating the corresponding nitroso compound either with stannous chloride and hydrochloric acid or with iron powder and dilute alcohol in the presence of a trace of hydrochloric acid, owing to side reactions, presumably, the anticipated amino compound was formed only in a poor yield, whereas the nitroso compound, on reduction by iron powder and dilute hydrochloric acid, gave the dihydroxyl compound in a satisfactory yield.

The diazo reaction which is not shown by the nitroso compound may serve as evidence that the nitroso radical, now introduced, occupies the position adjacent to the hydroxyl radical.

From 5-nitroso-8-hydroxyquinoline or *p*-nitrosophenol, by analogy, we could isolate the corresponding dihydroxyl compounds in satisfactory yields, while from p-nitrophenol, the corresponding aminophenol, and hydroquinone and from *o*-nitrophenol, *o*-aminophenol only could be isolated.

Experimental

7-Nitroso-5-acetyl-8-hydroxyquinoline.—On the gradual addition of a solution of sodium nitrite (3.2 g.) in water (30 cc.) to a solution of 5-acetyl-8-hydroxyquinoline (8 g.)[1] in a mixture of glacial acetic acid (25 g.) and water (35 cc.) at 0° with stirring, yellow crystals separated. They were filtered after being allowed to stand for several hours at the room temperature (yield, 7.8 g.) and carefully recrystallized from glacial acetic acid into yellowish-brown prisms which begin to decompose at 180° and decompose thoroughly at 190–195°. It is soluble in the usual organic solvents, water or dilute mineral acids. It gives a light brown color reaction with ferric chloride, but no color reaction with diazotized sulfanilic acid.

Anal. Calcd. for $C_{11}H_8O_3N_2$: N, 12.96. Found: N, 12.60.

7-Amino-5-acetyl-8-hydroxyquinoline.—7-Nitroso-5-acetyl-8-hydroxy-quinoline (2.5 g.) was reduced with stannous chloride (5.4 g.) and concd. hydrochloric acid (13 5 g.) in the presence of glacial acetic acid (30 g.), and the reduction product isolated in the usual way; yield, 0.7 g. It forms light yellow needles from ether, melting at 148–149° (dec.). It is soluble in the usual organic solvents.

Anal. Calcd. for $C_{11}H_{10}O_2N_2$: C, 65.35; H, 4.95; N, 13.86. Found: C, 65.56; H, 5.34; N, 13.59.

The picrate gives orange needles from alcohol, decomposing at 201–222°

Anal. Calcd. for $C_{11}H_{10}O_2N_2 \cdot C_6H_3O_7N_3$: N, 16.21. Found: N, 16.27.

The hydrochloride gives orange needles, sintering at 145°. It is easily soluble in water.

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[1] Matsumura, THIS JOURNAL, 52, 4433 (1930).

5-Acetyl-7,8-dihydroxyquinoline.—3.75 g. of 7-nitroso-5-acetyl-8-hydroxyquinoline was dissolved in a hot solution (95°) of 27 g. of concd. hydrochloric acid in 900 cc. of water, 5 g. of iron powder was then gradually added during one hour with constant agitation, and the agitation continued for one hour more at the same temperature. On concentrating the reaction fluid, after filtration, under diminished pressure, 3.25 g. of yellow needles of the hydrochloride separated out This was dissolved in water and on neutralization with sodium carbonate, the deep red free base separated. On drying in a desiccator, it lost its red color and became colorless. It crystallizes as colorless prisms from alcohol, m. p. 235 236°. On dissolving in dilute hydrochloric acid and alkalifying, the initial red-colored substance can be regenerated. The red substance, on recrystallization from hot water, gives scarlet red needles.

Anal. Water of crystallization. Calcd. for $C_{11}H_9O_3N \cdot 1.5\ H_2O$: H_2O, 11.74. Found: H_2O, 11.07.

The red substance, on recrystallization from dilute alcohol which contains some acetic acid, gives deep red prisms or columns; m. p. 241–242° (dec.). It contains no water of crystallization and does not decolorize on drying at 100° but gradually decolorizes near its melting point. Its mixed melting point with the colorless form is at 236–240". On working up its alcoholic solution, after treatment with sulfur dioxide or sodium hydrosulfite, the initial substance can be recovered. It is moderately soluble in the usual organic solvents, dilute mineral acid or alkali. The solution in concd. sulfuric acid is light yellow. It gives a deep green color reaction with ferric chloride and a red color reaction with diazotized sulfanilic acid, only in highly concentrated solution.

Anal. Calcd. for $C_{11}H_9O_3N$: C, 65.02; H, 4.43; N, 6.89. Found: C, 65.40; H, 4.89; N, 7.00, 6.55.

The hydrochloride gives lemon-yellow needles from hydrochloric acid (10%), m. p. 280–305° (decomp.). It is difficultly soluble in alcohol but easily soluble in water.

Anal. Calcd. for $C_{11}H_9O_3N \cdot HCl$: C, 55.12; H, 4.18; N, 5.85. Found: C, 55.41; H, 4.51; N, 5.83.

The oxime gives red needles from dilute alcohol which contains some acetic acid; these decompose at 215–220° without melting.

Anal. Calcd. for $C_{11}H_{10}O_3N_2$: N, 12.84. Found: N, 12.55.

5-Acetyl-7,8-diacetoxyquinoline.—A mixture of 0.2 g. of 5-acetyl-7,8-dihydroxyquinoline (red form), 0.5 g. of sodium acetate and 2 g. of acetate anhydride was heated on a water-bath for one hour. On pouring the cooled reaction fluid on crushed ice, colorless crystals separated. These were recrystallized from ether into colorless columns, m. p. 121–122°, yield, 0.2 g. It is easily soluble in alcohol, benzene, ether or dilute hydrochloric acid.

Anal. Calcd. for $C_{15}H_{13}O_5N$: C, 62.72; H, 4.57; N, 4.88. Found: C, 62.59; H, 5.00; N, 4.97.

5,8-Dihydroxyquinoline.—2.85 grams of 5-nitroso-8-hydroxyquinoline was reduced in exactly the same manner that was described for 5-acetyl-7,8-dihydroxyquinoline, and 2.85 g. of orange needles of the hydroxychloride obtained. The free base gives colorless needles from benzene, m. p. 181–183".

Anal. Calcd. for $C_9H_7O_2N$: N, 8.70. Found: N, 9.01.

The sulfate gives orange needles from water and begins to decompose at 250°.

Hydroquinone.—Two grams of *p*-nitrosophenol was reduced in the way described above, except that the reaction mixture, on cooling, was directly shaken six times with ether. On evaporating the solvent, after decolorization with animal charcoal, 1 g. of light brown colored needles of hydroquinone was obtained, and recrystallized from hot water, m. p. 169–171°.

Anal. Calcd. for $C_6H_6O_2$: C, 65.45; H, 5.45. Found: C, 65.31; H, 5.46.

The mother liquor, after being made alkaline with sodium carbonate, was shaken six times with ether. On evaporating the solvent, 0.02 g. of almost colorless leaflets was obtained which after treatment with alcohol melted at 187–188°, and gave, in contact with calcium hypochlorite, color reactions specific to p-aminophenol.

Anal. Calcd. for C_6H_7ON: N, 12.84. Found: N, 12.94.

TABLE I

REDUCTION OF NITROPHENOL

Reactant	G.	Products	Yield, g.	M. p., and mixed m. p., °C.
p-Nitrophenol	2.8	Hydroquinone	0.45	169–170
		p-Aminophenol	.90	187
o-Nitrophenol	2.8	o-Aminophenol	1.65	179

The writers, hereby, desire to express their hearty thanks to Professor Hata for the interest which he has kindly taken in this work, and to Professor H. T. Clarke of Columbia University for his criticisms given to this article.

Summary

By reduction of nitrosophenols by iron and hydrochloric acid, the following compounds have been prepared: 5-acetyl-7,8-dihydroxyquinoline, 5,8-dihydroxyquinoline and hydroquinone.

TOKYO, JAPAN

[CONTRIBUTION FROM THE RESEARCH LABORATORY, CHEMISTRY DEPARTMENT, UNIVERSITY OF THE PHILIPPINES]

PHENOLIC DECOMPOSITION OF CERTAIN MIXED ETHERS. II. THE EFFECT OF SUBSTITUTION. THE RATE CONSTANT

BY D. M. BIROSEL

RECEIVED AUGUST 25, 1930 PUBLISHED APRIL 6, 1931

In the first paper[1] of this series it was pointed out that the phenolic decomposition of mixed ethers is influenced by a number of factors. In the present investigation, the influence of substitution in the phenyl residue upon the decomposition of certain mixed ethers by hydrogen bromide in glacial acetic acid at the temperature of the steam-bath has been determined.

Experimental

Preparation of Materials.—When it was possible, the procedure adopted by Claisen[2] in preparing phenyl allyl ethers was followed to synthesize the mixed ethers used in this investigation. The scheme of procedure is

$$C_6H_5OH + C_3H_5I + K_2CO_3 \longrightarrow C_6H_5OC_3H_5 + KI + KHCO_3$$

Birosel, THIS JOURNAL, 52, 1944 (1930).

[2] Claisen, Ber., 45,3157 (1912); Ann., 401, 21 (1913); *ibid.*, 418, 69 (1919).

Claisen recommended a non-dissociating solvent for this reaction; otherwise, one obtains the isomeric phenol instead of the ether. Acetone was used in all the preparations. The above equation calls for a monomolecular proportion of the active components but in practice alkyl halide and anhydrous potassium carbonate are taken in excess of the theoretical amount. The mixture is digested on the water-bath at the boiling temperature of acetone in a reflux condenser during a period of from six to eight hours. At the end of the digestion, water is added to the mixture to dissolve the solid carbonate and the product separates as liquid which is

TABLE I

PREPARATIONAL DATA OF THE PHENETOLES

Reagent *-Phenol*	*g.*	EtI, g.	K_2CO_3, *g.*	*Acetone, cc.*	Crystals Prom	Form	M. p., °C.	*Yield* g.	%	*Ref.*
o-Nitro-	8.5	14	13	40	EtOH	Prisms	57.8	3	29	1
p-Chloro-	29	38	50	50	Liquid, b. p.		210–212	23	74	2
p-Bromo-	10	15	10	25	Liquid, b. p.		228	..	100	3
p-Cresol	12	12	20	40	Liquid, b. p.		186–188	12	79	4
2,4-Dibromo-[a]	7	9	8	40	Liquid, b. p.		266–268	..	99	5
					EtOH	Rhombs	53–54	..	...	
2,4-Dichloro-	10	20	12	40	Liquid, b. p.		235–236	10.6	90	6
2,4,6-Tribromo	6	6	4	40	EtOH	Needles	71–72	..	100	7
Silver picrate	..	..	..	..	EtOH	Needles	78.5	..	....	8

[a] From phenolic decomposition of 2,4-dibromoanisole (m. p. 63°).

(1) Fritzsche, *Ann.*, 110, 166 (1859), prepared *p*-nitrophenyl ethyl ether from the silver salt of *p*-nitrophenol and ethyl iodide; prismatic crystals from ether, m. p. 57–58".

(2) Beilstein and Karbatow, ibid., 176, 30 (1875), prepared *p*-chlorophenyl ethyl ether by digesting equivalent amounts of p-chlorophenol, ethyl iodide and potassium hydroxide; b. p. 210–212°.

(3) Lippmann, *Jahrsb. Chem.*, 548 (1870), made *p*-bromophenyl ethyl ether from ethyl bromide and potassium p-bromophenolate; oil, b. p. 233°. Autenrieth and Miihlinghaus, *Ber.*, 39, 4098 (1906), from phenetole and phosphorus pentabromide; liquid, b. p. 225–226°.

(4) Pinette, *Ann.*, 243, 41 (1888), obtained *p*-cresyl ethyl ether by digesting *p*-cresol with alcoholic potash and ethyl iodide; oil, b. p. 189.9°. Englehardt and Latschinow, *Z. Chem.*, 619 (1869), reported b. p. 186–188°.

(5) Autenreith and Miihlinghaus, *Ber.*, 39, 4098 (1906), prepared 2,4-dibromophenyl ethyl ether from phenetole and phosphorus pentabromide; large rhombs, m. p. 50°. Pope, J. *Chem. Soc.*, 101, 1823 (1912), from 2,4-dibromophenol, alcoholic potash and ethyl iodide; rhombic plates, m. p. 53.3°. Lippmann, *Jahrsb. Chem.*, 739 (1870), from phenetole and two moles of bromine.

(6) Fischer, *Ann. Suppl.*, 7, 183 (1870); oil, b. p. 236–237°.

(7) Raiford and Birosel, THIS JOURNAL, 51,1776 (1929), from phenetole and three moles of bromine in chloroform; needles from alcohol, m. p. 69°. Purgotti, *Gazz. chim. ital.*, 16, 528 (1886), from silver 2,4,6-tribromophenolate and ethyl iodide; m. p. 69°. Varda, *ibid.*, 23,494 (1893), from the potassium salt; m. p. 72–73'.

(8) Willgerodt, *Ber.*, 12, 1277 (1879), prepared 2,4,6-trinitrophenyl ethyl ether from alcoholic potash and picryl chloride; needles, m. p. 78°. Miiller and Stenhouse, *Ann.*, **141,** 80 (1867), from silver picrate and ethyl iodide; needles, m. p. 78.5".

extracted with ether. The ether solution is separated, washed with dilute sodium hydroxide, and then with distilled water. The ether solution is dried with anhydrous sodium carbonate and filtered. The solvent is evaporated and if the residue is a liquid it is distilled and the portion which boils over at the temperature recorded in the literature for the particular compound is reserved for use. When the residue is a solid, it is crystallized from the appropriate solvent and the melting point and crystalline form are noted.

2,4,6-Trinitrophenetole.—Attempts to prepare this compound by Claisen's and Willgerodt's methods, respectively, were unsuccessful. The ether was successfully synthesized by following the method adopted by Raiford and Birosel (Ref. 7, Table I) in preparing 2,4,6-trinitrophenyl allyl ether. Silver picrate prepared from the ammonium salt was digested with ethyl iodide using acetate as reaction medium. During the course of digestion yellow silver iodide salt was precipitated. When digestion was complete, the salt was filtered and washed with acetone. The solvent was evaporated and the solid residue was dissolved in ether. The ether solution was washed with dilute sodium hydroxide, then with distilled water. The solvent was evaporated and the residue was crystallized from ethyl alcohol.

Procedure of Decomposition.—The extent of the phenolic decomposition of the mixed ethers recorded above and velocity constants were determined at the temperature of the steam-bath by a reflux condenser. The procedure is the same as that followed in a previous work.' The acid

TABLE II

EXTENT OF DECOMPOSITION OF CERTAIN MIXED ETHERS

Expt.	Compound, ethyl ether	Time, min.	Ether used, g.	Acid soln., cc.	Phenol obtained, g.	Decomposition, %
1	p-Nitrophenyl	120	0.5000	30	0.0660	13.20
2	p-Chlorophenyl	120	1.0410	30	.7488	85.28
3	p-Bromophenyl	120	1.0540	30	.7792	85.95
4	*p*-Methylphenyl	120	1.4010	30	.5000	44 95
5	2,4-Dibromophenyl	120	0.5000	30	.2726	60.59
6	2,4-Dichlorophenyl	120	1.0180	30	.4644	40.35
7	2,4,6-Tribromophenyl	120	0.5000	30	.1000	21.78
8	2,4,6-Trinitrophenyl	120	.5000	30	Complete decomposition	

TABLE III

RATE OF DECOMPOSITION OF 2,4,6-TRIBROMOPHENYL ETHYL ETHER IN GLACIAL ACETIC ACID MEDIUM

Expt.	Time, min.	Ether used, g.	Acid solu., cc.	Tribromophenol[a] obtained, g.	Calcd. amount of dec. ether, g.	Decomposition, %	$K \times 10^{-3}$
1	30	0.5000	30	0.0340	0.0369	7.40	2.56
2	60	.5000	30	.0620	.0672	13.50	2.42
3	90	.5000	30	.0840	.0911	18.29	2.24
4	120	.5000	30	.1000	.1085	21.78	2.25
5	150	.5000	30	.1130	.1225	24.60	2.02

[a] Crystallization from alcohol gave fine needle crystals melting at 92°. No depression in melting point was noted when it was mixed with the original tribromophenol

TABLE IV

RATE OF DECOMPOSITION OF CERTAIN MIXED ETHERS IN GLACIAL ACETIC ACID AS REACTION MEDIUM

Expt.	Compound, ethyl ether	Time, min.	Ether used, g.	Acid soln., cc.	Phenol obtained, g.	Calcd. amount of dec. ether, g.	Velocity constant $K \times 10^{-3}$
2	*p*-Nitrophenyl	60	0.5000	30	00316	0.0380	1.28
		120	.5000	30	.0549	.0660	1.18
3	*p*-Bromophenyl	30	1.2185	30	.3935	.4573	15.68
		60	1.3350	30	.6920	.8042	15.48
		120	1.0540	30	.7792	.8955	15.79
3	*p*-Chlorophenyl	30	1.0035	30	.3140	.3727	15.14
		60	1.0410	30	.5380	.6385	15.77
		120	1.0410	30	.7488	.8770	15.38
2	*p*-Methylphenyl	30	0.9190	30	.1000	.1259	4.91
		60	1.3240	30	.2650	.3337	4.84
		120	1.4010	30	.5000	.6297	4.97
3	2,4-Dibromophenyl[a]	30	0.5000	30	.0925	.1028	7.67
		90	.5000	30	.2200	.2556	7.95
		120	.5000	30	.2726	.3030	7.84

[a] A nitro derivative, 2,4-dibromo-6-nitrophenol was prepared according to the directions of Kohn and Dömötör, *Monatsh.*, 48,211 (1927), from the dibromophenol obtained from the phenolic decomposition of 2,4-dibromophenyl ethyl ether; crystallization from alcohol gave small yellow plate crystals melting at 118°.

solution used in this present investigation was made in the same proportion as the material used in former work; one volume of constant boiling hydrobromic acid was added to two volumes of glacial acetic acid. The results obtained from experiments are given in the tables.

Discussion

In Table II are given the detailed results of experiments on the extent of decomposition of eight derivatives of phenyl ethyl ether by constant boiling hydrobromic acid in glacial acetic acid as reaction medium. The influence of substitution was determined with particular regard to four different radicals: nitro, chloro, bromo and methyl replacing the hydrogen atom attached to the p-carbon atom of the benzene nucleus. Comparing the figures obtained from experiments for the extent of decomposition of the mono substituted derivatives of phenetole, the influence of substitution is very apparent. When the substituting group is multiplied in the phenyl residue, the extent of the phenolic decomposition of certain mixed ethers decreases in magnitude. When *p*-bromophenyl ethyl ether was subjected to the action of constant boiling hydrobromic acid in glacial acetic acid as reaction medium at the temperature of the stem-bath for two hours, the decomposition was 85.95% complete; for 2,4-dibromophenyl ethyl ether the extent of decomposition is 60.59%; and for 2,4,6-tribromophenyl ethyl ether the magnitude of decomposition has decreased to 21.78%

which is about one-fourth the magnitude of the value obtained for the monobromo derivative. p-Chlorophenyl ethyl ether was decomposed to the extent of 85.28%, while the dichloro derivative for the same interval of time was only decomposed 40.35%, which is less than one-half of the value obtained for the monochloro derivative. The result for 2,4,6-trinitrophenyl ethyl ether shows that the compound is not stable toward hydrogen bromide.

In Table III are shown the results of the experiments on the velocity constant of the phenolic decomposition of 2,4,6-tribromophenyl ethyl ether at the temperature of the steam-bath. The rate constants K are those calculated from the integrated form of the differential equation for the first order reactions, using logarithms to the base e. It will be noted that the constancy of k is quite satisfactory. The calculated amount of decomposed ether was obtained by multiplying the amount of tribromophenol directly determined from experiment by the factor 1.0847.

In Table IV are recorded the rate constants of the phenolic decomposition of p-nitro-, p-bromo-, p-chloro-, p-methyl and 2,4-dibromophenyl ethyl ethers. The figures obtained for each compound from two or three experiments are in close agreement. The monohalogen derivatives give much higher rate constants than either the mononitro or monomethylphenyl ethyl ether. The magnitude of the rate constant is decreased when the same halogen substituent is multiplied in the phenyl residue. Comparing the velocity constants obtained for monobromo, dibromo and tribromo phenetoles, it appears that the rate constant is also dependent upon the number of substituents actually present in the benzene nucleus.

Summary

1. The kinetics of the phenolic decomposition of mixed ethers have been studied further in the case of 2,4,6-tribromophenyl ethyl ether and to a less extent with the case of p-nitro-, *p*-bromo-, p-chloro-, *p*-methyl- and 2,4-dibromophenyl ethyl ethers. Experiments were made in glacial acetic acid as reaction medium.

2. The rate constants of 2,4,6-tribromophenyl ethyl ether and of the other compounds were calculated from the experimental results and their constancy is quite satisfactory. The phenolic decomposition of mixed ethers appears to be a first order reaction.

3. The rate constant is influenced by the number of substituents actually present in the phenyl residue.

4. The phenolic decomposition of mixed ethers is influenced by the substituting group present in the benzene nucleus.

The influence of position of substitution on the phenolic decomposition of mixed ethers is being studied.

MANILA, PHILIPPINE ISLANDS

[CONTRIBUTION FROM THE RESEARCH LABORATORY, THE UPJOHN COMPANY]

ERGOSTENOL CHLOROACETATE

BY MERRILL C. HART AND FREDERICK W. HEYL

RECEIVED NOVEMBER 5, 1930 PUBLISHED APRIL 6, 1931

Windaus and Grosskopf[1] catalytically reduced ergosterol from yeast and obtained the tetrahydro reduction product, a-ergostenol, to which, however, they assigned the hexahydro, or completely reduced formula and corresponding name, *i. e.*, ergostanol. Reindel and Walter[2] made a number of quantitative reductions and demonstrated that the catalytic reduction of ergosterol acetate with Willstatter's platinum black gave the tetrahydro derivative, a-ergostenol. This substance, according to Windaus and Lüttringhaus,[3] melts at 131°, $[\alpha]_D$ +11.4°; and a-ergostenol acetate, m. p. 109–110°, $[\alpha]_D$ 0°. Hart, Speer and Heyl[4] reported a-ergostenol, m. p. 133°, $[\alpha]_D$ +10.5°; a-ergostenol acetate, m. p. 110–111°, $[\alpha]_D$ 0°.

Reindel and Walter stated further that the reduction of ergosterol acetate in ether with Adams' platinum oxide catalyst gave a hexahydro derivative, but this has since been shown to be incorrect,[5] the mixture actually containing dihydro-ergosterol.

Reindel, Walter and Rauch[6] state that chloroacetyl chloride reacts with a-ergostenol to form β-ergostenol chloroacetate, m. p. 167°. The β-form is characterized by easy reducibility to a hexahydro-ergosterol. This hexahydro-ergosterol, which is a well-known derivative, is known as allo-α-ergostanol. In a previous paper[4] we have prepared so-called β-ergostenol chloroacetate and reported that upon saponification a mixture of alcohols melting at 110–112° was obtained.

In the present paper we describe the fractional crystallization of the chloroacetate prepared from a-ergostenol. This work was undertaken for the purpose of preparing pure β-ergostenol, which should, of course, be readily prepared from the β-chloroacetate.

Although a careful fractionation of a-ergostenol acetate failed to reveal lack of uniformity in the product obtained by the catalytic reduction of ergosterol, we found that the fractionation of the chloroacetate yielded small amounts of allo-a-ergostanol. Furthermore, ergostenol chloroacetate was found to consist largely of the a-isomer and not exclusively of the β-form as Reindel states. The chloroacetates contain, in addition to allo-a-ergostanol, a-ergostenol chloroacetate, β-ergostenol chloroacetate and an addition product, $C_{31}H_{49}O_3Cl_3$.

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[1] Windaus and Grosskopf, *Z. physiol.* Chem., 124, 8 (1923).

[2] Reindel and Walter, Ann., 460, 212 (1928).

[3] Windaus and Lüttringhaus, *ibid.*, 481, 119 (1930).

[4] Hart, Speer and Heyl, THIS JOURNAL, 52, 2016 (1930).

[5] Reindel and Detzel, *Ann.*, 475, 80 (1929).

[6] Reindel, Walter and Rauch, *ibid.*, 452, 34 (1927).

We have not been able to isolate pure β-ergostenol. That it is present is shown by the fact that upon catalytic reduction an increased amount of allo-a-ergostanol can be secured from the mixture of chloroacetates.

Attempts to separate a derivative of β-ergostenol from the mixture of the chloroacetates, by bromination or by oxidation with benzoyl hydroperoxide[7] failed to lead to any derivatives which might be characteristic for the β-form as contrasted with the a-form. One might expect, for example, to secure from an unsaturated sterol, which is readily reduced, either a dibromide or a peroxide.

Experimental

Fractionation of **Ergostenol Chloroacetate.**—Ergostenol chloroacetate was prepared from 25.6 g. of a-ergostenol (m. p. 132–133°) by gently refluxing with an excess of chloroacetyl chloride for twenty minutes. Hot acetic acid was added and the mixture stood aside to crystallize. The top fraction after five crystallizations from acetic acid weighed 16.1 g., m. p. 166–167°, and $[\alpha]^{22}_D$ +6.93.

Anal. Calcd. for $C_{29}H_{42}O_2Cl$: Cl, 7.66. Found: Cl, 7.71.

This material was systematically crystallized ten times from ethyl ether with the results shown in Table I.

TABLE I

FRACTIONATION OF ERGOSTENOL CHLOROACETATE

Fraction no.	Weight, g.	$[\alpha]_D$	M. p., °C.
1	0.909	+ 5.3	190–192
2	0.715	+ 5.5	169–170
3	1.187	+ 6.24	169–170
4	2.216	+ 4.86	168–169
5	3.650	+ 6.24	167–168
6	3.452	+ 6.94	165–166
7	2.490	+15.56	162–164
8	0.548	+20.82	153–156

Fraction 1 is practically pure allo-α-ergostenol; recrystallized from ether, m. p. 199–200°; $[\alpha]_D$ +2.3°. Reindel gives 200–201°. Upon saponification and subsequent acetylation pure allo-a-ergostanol acetate, m. p. 149–149.5°, was obtained.

Anal. Calcd. for $C_{27}H_{47}OCOCH_3$: C, 80.9; H, 11.7. Found: C, 81.0; H, 11.5.

The alcohol itself melted at 144°. Reindel gives 144–145°. The isolation of allo-α-ergostanol chloroacetate from the most insoluble fraction proves that the reduction of ergosterol acetate in acetic acid solution with platinum oxide (Adams') as a catalyst results in the formation of small amounts of the hexahydro derivative, allo-α-ergostanol.

Fractions 2 to 8 of the chloroacetate crystallization were separately saponified and the fractions showed melting points that varied from 118–120° to 129–131°, while the rotations varied from +11.8 to +17.3°. All these rotations are considerably higher than that required for α-ergostenol, and those fractions showing a rotation considerably higher than that reported by Reindel for β-ergostenol (+15.9°) were obviously mixtures. It may be predicted safely that β-ergostenol, when finally isolated, will show a higher positive specific rotation than +17.3°.

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[7] Westphalen, Ber., 48, 1064 (1915).

In these fractions the a-isomer so largely predominated that it was possible to isolate it in comparatively pure form as the characteristic plates of the acetate. Fractions in which the a-form was present in much smaller amounts yielded acetatcs crystallizing in needles. The elementary composition of the fractions agreed with that required for $C_{29}H_{48}O_2$.

Isolation of ***an*** Addition Product of a-Ergostend Chloroacetate and Chloroacetyl Chloride.—During the main crystallizations of ergostenol chloroacetate, in addition to the top fraction weighing 16.1 g. and melting at 166–167°, four other fractions of ergostenol chloroacetate were obtained. These fractions melted at 157–159°, 144-147', 107–110° and 110–114°. The first three of these fractions were exhaustively fractionated from ethyl acetate, acetone and ether and various fractions melting from 110–160° were obtained.

The lowest fraction of ergostenol chloroacetate crystallization (m. p. 110–114°) was treated with hot alcohol. The material insoluble in the hot alcohol was crystallized twice from acetone and once from acetic acid; 0.3 g. of irregular plates melting at 129–130" were obtained, [a], +8.7°.

Anal, Calcd. for $C_{31}H_{49}O_3Cl_3$: Cl, 18.5. Found: Cl, 17.0, 17.3.

This substance on saponification from 3% methyl alcoholic and crystallization from alcoholic solution gave needles of a-ergostenol melting at 132–133°. The acetatcs prepared from acetic anhydride crystallized in plates melting at 110–111°. Mixed melting points with a-ergostenol and a-ergostenol acetate, respectively, were not depressed.

Catalytic Reduction of Ergostenol **Chloroacetate.**—Six grams of ergostenol chloroacetate, m. p. 166–167°, was reduced in acetic acid solution with Adams' platinum oxide as catalyst. The reduced chloroacetate after several crystallizations from ether, acetic anhydride and acetic acid, melted at 184–186°, and on saponification with 5% methyl alcoholic potash and after four crystallizations from alcohol and ether gave crystalline plates of allo-a-ergostanol melting at 144–145°, yield 1.1 g. The acetate crystallized in plates melting at 149–149.5°, $[\alpha]_D$ +4.7°. The benzoate prepared by means of benzoyl chloride and pyridine melted at 163–164°.

Attempt to Isolate a Bromide from the Isomerization Mixture.——When ergostenol chloroacetate (5.95 g.) in 450 cc. of ether was treated with 24 cc. of 9% bromine solution, no insoluble bromide separated. The yellow ether solution was washed with 10% sodium thiosulfate solution and water and then dried over anhydrous sodium sulfate. The product was free from bromine. It was saponified with methyl alcoholic potash and an extremely small yield of crystalline plates that melted at 144–145° was obtained. This in no way represented any characteristic derivative which should be useful in working with this mixture. Upon analysis it showed the composition of an oxidation product, $C_{27}H_{43}OH$. The acetate formed plates melting at 145–146".

Anal. Calcd. for $C_{29}H_{46}O_2$: C, 81.6; H, 10.9. Found: C, 81.7; H, 11.0.

It gave a-ergostenol acetate upon catalytic reduction. This is undoubtedly a dehydro-ergostenol but it shows a rather wide divergence from the compound isolated by Windaus and Lüttringhaus[3] by the action of bromine or benzoyl hydroperoxide on α-ergostenol acetate. They found 135–136° for the melting point of the acetate of their dehydro compound and 141° for that of the alcohol. We attempted to establish the identity of our product by preparing the dehydro derivative by the action of benzoyl hydroperoxide[8] on a-ergostenol acetate. Similarly a slight yield of a dehydro derivative, the acetate of which melted at 145–146°, was obtained (C, 81.8; H, 10.9). When this acetate was mixed with the acetate obtained by the action of bromine on the chloroacetate as described above there was no depression of the mixed melting point.

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[8] Baeyer and Villiger, *Ber.*, **33**, 1569 (1900).

Summary

1. a-Ergostenol, prepared by the catalytic reduction of ergosterol acetate in acetic acid solution with platinum oxide (Adams') as a catalyst, contains small amounts of allo-a-ergostanol.

2. Ergostenol chloroacetate was found to be very largely a-ergostenol chloroacetate with smaller amounts of the chloroacetates of β-ergostenol and of allo-a-ergostanol.

3. Ergostenol reacts with chloroacetyl chloride to form, in small amount, an addition product, $C_{31}H_{49}O_3Cl_3$.

4. Ergostenol chloroacetate forms neither a bromide nor a peroxide nor does it react with potassium permanganate. Upon reduction evidence of some degree of isomerization is found in the increased yield of the reduction product, allo-a-ergostanol.

KALAMAZOO, MICHIGAN

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE PREPARATION OF DIMETHYLACETOACETIC ESTER AND OF Δ^3,2,2-DIMETHYLBUTENOL-1

BY KARL FOLKERS AND HOMER ADKINS

RECEIVED NOVEMBER 6, 1930 PUBLISHED APRIL 6, 1931

A considerable quantity of A^3,2,2-dimethylbutenol-1 was desired in order to study its behavior over oxide catalysts.' It appeared that this compound could be most easily prepared from acetoacetic ester through the following series of compounds: (1) monomethylacetoacetic ester, (2) dimethylacetoacetic ester, (3) 3-hydroxy-2,2-dimethylbutyric ester, (4) A^3,2,2-dimethylbutyric ester, (5) Δ^3,2,2-dimethylbutenol-1.

There does not seem to be available in the literature adequate directions for the methylation of acetoacetic ester, although the two derivatives have been prepared in a more or less pure state by a number of investigator~.The method of preparation described below has been developed.

Ethyl 2-Methylacetoacetate.—Thirty-nine and eight-tenths grams (1.73 moles) of sodium was very finely powdered in xylene so that it was like sand. After decanting the xylene, the sodium was washed with two 75-ml. portions of dry toluene (Note **1).** The sodium was then covered with one liter of dry toluene, and the flask fitted with a **reflux** condenser, immersed in an ice-bath, and allowed to cool for fifteen minutes, after which **218.3** g. (1.68 moles) of ethyl acetoacetate (Note 2) was added down the condenser during the course of ten to fifteen minutes (Note **3)** while the flask was vigorously shaken and kept in the ice-bath. The top of the condenser was now fitted with a calcium chloride tube and, after an additional ten minutes' cooling, was allowed to stand at room

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[1] Adkins and Folkers, THIS JOURNAL, 53, **1095 (1931).**

[2] Frankland and Duppa, ***Ann.*, 138, 328 (1860);** Conrad and Limpach, *ibid.*, 192,153 **(1878);** Michael, ***Ber.*, 38,2083 (1905);** Clark, **THIS JOURNAL, 33,527 (1911).**

temperature for seven to ten hours, with an occasional vigorous shaking during the first hour. The reflux condenser was then temporarily removed, a long-stem funnel pushed down into the semi-solid salt, and 253 g. (1.78 moles) of methyl iodide added. After standing overnight, the flask was heated on the steam-bath for four to six hours with an occasional vigorous shaking. The sodium iodide settled out completely at the end of this time. The sodium iodide was then filtered off with suction through a 20-cm. Büchner funnel (Note 4). The filter cake was pressed with a cork and sucked as dry as possible. The filtrate was then fractionated through a 25-cm. Widmer column. The toluene was conveniently fractionated at about 250 mm. pressure, or at atmospheric pressure with the use of a heater around the column. The yield of ethyl 2-methylacetoacetate was 170 g. (70–71%) (Note 5), boiling at 75–76' at 15 mm.

Ethyl 2,2-Dimethylacetoacetate.—The sodium salt of ethyl 2-methylacetoacetate was prepared as above using 35.6 g. (1.55 moles) of sodium, 216 g. (1.50 moles) of ethyl 2-methylacetoacetate and one liter of dry toluene. After adding 227 g. (1.6 moles) of methyl iodide and allowing to stand overnight, the flask was heated for fourteen hours on the steam-bath with a vigorous shaking every other hour. Because the closeness of the boiling points of the mono- and dimethylacetoacetic esters makes fractionation impossible, the di-substituted ester was purified by treatment with more sodium and methyl iodide to react with the mono-substituted ester (Note 6). To carry out this purification the sodium iodide was next filtered, and the filtrate distilled through a 25-cm. Widmer column until approximately 350 ml. of distillate had been collected and the temperature of the vapor was 109–110°. This distillate was chiefly toluene, with a little water and the greater portion of the lower-boiling by-products. Then, assuming the presence of 1.1 moles of substituted acetoacetic ester (75% of the original 1.5 moles), 10% of which is the monomethyl derivative, the distillation residue was added to this calculated amount of powdered sodium (2.5 g.). The flask was fitted under a reflux condenser, and after standing from four to five hours, 7 ml. of methyl iodide added. After standing overnight and a half hour's heating on the steam-bath, the reaction was complete. The sodium iodide was then filtered off and the toluene and ester fractionated through a Widmer column. The yield of ethyl 2,2-dimethylacetoacetate was 128 g. (54% of the theoretical amount based on ethyl 2-methylacetoacetate) and boiled at 72–73" at 14 mm.

Notes.—1. Due to the closeness of the boiling points of xylene and the mono- and dimethyl substituted acetoacetic esters, the fractionation of the product is facilitated by washing out all of the xylene. Absolute ethanol may be used in the preparation of the monomethyl substituted ester (70% yields) as the solvent; however, the high solubility of sodium iodide in alcohol makes its removal very difficult. Benzene may be used as the solvent to prepare the monomethyl substituted ester in 70–80% yields and the dimethyl substituted ester in 50–60% yields (without purification); however, the use of ordinary benzene (or toluene) containing thiophene introduces sulfur-containing compounds into the product, which make it impractical to reduce the ester over a nickel catalyst. Mallinckrodt's c. p. quality toluene was distilled, until the distillate was no longer turbid, before using as the solvent.

2. Ethyl acetoacetate, b. p. 70° (16 mm.) from the U. S. Industrial Alcohol Company was redistilled before using.

3. No difficulty was encountered in agitating the bulky sodium salt, if the ester was added quite rapidly and the solution kept well cooled. If the ester was added more slowly, the salt became too solid for thorough mixing before all of the ester could be added. The sodium salt prepared in this manner had a bluish-white color.

4. The finely divided sodium iodide precipitate was easily filtered if a 25-cm. filter paper was used in a 20-cm. funnel, the edge of the paper being held to the side of the funnel with gummed paper.

5. By cutting the fractionation of the toluene solution at 71–72° at 14 mm., 78% yields of crude ethyl 2-methylacetoacetate map be obtained, and used directly for the preparation of the dimethyl substituted ester in 50% yields.

6. This method of purification gave a product which showed a slight test for enol with ferric chloride, indicating the presence of some monomethyl substituted ester.

Ethyl **2,2-dimethyl-3-hydroxybutyrate**, b. p. 94–95' (21 mm.), was obtained in 88–93% yields by the reduction with a nickel catalyst of ethyl 2,2-dimethylacetoacetate.[3]

Ethyl **Δ^3,2,2-dimethylbutyrate**, b. p. 139–141°, was obtained in 74–80% yields by the dehydration of ethyl 2,2-dimethyl-3-hydroxybutyrate with phosphorus pentoxide.[4]

Δ^3,2,2-Dimethylbutenol-1.—Courtot[5] stated that he reduced ethyl Δ^3,2,2-dimethylbutyrate with sodium and ethanol by the method of Bouveault and Blanc but gives no further information on the preparation. At least three modifications of the procedure of Bouveault and Blanc have been proposed as advantageous for the reduction of various esters to the corresponding alcohols through the use of sodium and ethanol. Levene and Allen[6] used a hydrocarbon (toluene) as a reaction medium, and added the ester slowly to the sodium completing the reaction in one hour. Adams and Marvel[7] did not use a hydrocarbon solvent and added the sodium as rapidly as possible (one hour) to the ester. Ford and Marvel[8] used a hydrocarbon as a reaction medium and added the ester very rapidly (two to five minutes) to the sodium.

The methods of Adams and Marvel and of Ford and Marvel were compared for the reduction of the ethyl Δ^3,2,2-dimethylbutyrate, and it was found that the method of adding the ester rapidly to powdered sodium in a hydrocarbon medium (methylcyclohexane) was very much inferior to that of Adams and Marvel in that the yield of alcohol was only 25% and in that the corresponding acid was produced in large amounts, *i. e.*, 48%. The low yield of alcohol and the high yield of acid was not due to the quality of the reagents, because the same materials were used in the procedure described below.

The preferred method for carrying out the reduction was as follows. One hundred and thirteen grams (0.8 mole) of ethyl Δ^3,2,2-dimethylbutyrate and 927 ml. of absolute ethanol (dried once over lime and twice over magnesium methoxide) were placed in a three-necked, 5-liter flask, which was fitted with a rapid mechanical stirrer and *a* condenser 85 cm. in length and of 2.5 cm. bore. Through the other neck was added 110.5 g. (4.8 moles) of sodium in small pieces during the course of fifty minutes. At the end of this time only a few pin heads of sodium remained, which were dissolved after five minutes. A small flame was used toward the end of the addition to keep the solution hot enough so that the sodium remained melted. The color of the solution was now only light yellow. While still hot, the solution was poured into a 3-liter flask fitted with a 25-cm. Widmer column and 300 ml. of ethanol was distilled (oil-bath, 140–170°). Then 500 ml. of water (part of which was used to rinse out

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[3] Adkins, Connor and Cramer, THIS JOURNAL, **52,** 5195 (1930).

[4] Courtot, *Bull. soc. chim.*, 35, 111–113 (1906).

[5] Courtot, Ref. 4, p. 121.

[6] Levene and Allen, *J. Biol. Chem.*, 27, 443 (1916).

[7] Adams and Marvel, THIS JOURNAL, 42, 315 (1920).

[8] Ford and Marvel, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1930, Vol. X, p. 62.

the reaction flask) was cautiously added. The distillation was continued until the vapors were at 83.5° and 687 ml. of distillate was collected.

Since some A^{S},2,2-dimethylbutenol-1 distilled over with this aqueous ethanol, it was recovered by adding 150 ml. of water to the 687 ml. of distillate and distilling this mixture through a 50-cm. Widmer column until the vapors were at 84°. The residue (about 150 ml.) was transferred to an ordinary 500-ml. distilling flask and distilled. Two 25-ml. portions of distillate were collected. Each of these was salted out with anhydrous potassium carbonate to give about 15 ml. (total) of ethanol and the unsaturated alcohol, which was added to the bulk of the alcohol before drying. The original distillation residue was steam distilled until about 300 ml. of distillate was collected. The alcohol layer was separated. The water layer was treated with potassium carbonate and distilled after removal of the alcohol layer. Twenty-five ml. distillates were collected and salted out until all the alcohol had been obtained. All the alcohol layers were combined and dried twice over anhydrous potassium carbonate. Ether was used as a solvent to prevent mechanical loss. The yield of Δ^{3},2,2-dimethylbutenol-1, b. p. 128.5–131°, on fractionation through a 20-cm. Widmer column was 49.5 g. or 61.8% of the theoretical. The steam distillation residue, after removal of the alcohol, contained only very little non-volatile insoluble material. It was acidified with sulfuric acid and the Δ^{3},2,2-dimethylbutyric acid was steam distilled. The entire distillate was just neutralized with a sodium hydroxide solution and evaporated to dryness. The yield of sodium A^{3},2,2-dimethylbutyrate, dried to constant weight at 125°, was 8.6 g. or 7.9%.

Summary

Procedures are described for the preparation in good yields of dimethylacetoacetic ester from acetoacetic ester and for the reduction with sodium and ethanol of A^{3},2,2-dimethylbutyric ester to **A^{3},2,2-dimethylbutenol-1.** In the latter preparation the method of Adams and Marvel for the reduction of esters is shown to be very much superior to that which Ford and Marvel found to be advantageous in several such reductions.

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[A Communication from the Laboratory of Organic Chemistry of the University of Wisconsin]

CATALYSIS BY ALUMINA AND ZINC OXIDE OF THE DISPROPORTIONATION OF CERTAIN ALCOHOLS, ETHERS AND HYDROXY ESTERS

By Homer Adkins and Karl Folkers

Received November 6, 1930 Published April 6, 1931

It has been shown in previous papers[1] that over alumina allyl alcohol apparently undergoes intramolecular rearrangement to form propionaldehyde according to equation (I).

$$CH_2{=}CHCH_2OH = CH_3CH_2CHO \qquad (I)$$

It has also been demonstrated that alumina and zinc oxide may catalyze the reduction by alcohols of 2,3-unsaturated aldehydes such as acrolein and cinnamic aldehyde to the corresponding saturated aldehydes as indicated in equation (II).

$$CH_2{=}CHCHO + RCH_2OH = CH_3CH_2CHO + RCHO \qquad (II)$$

In connection with a study of the mechanism of the reactions of various organic compounds over oxide catalysts, it was considered of some importance to ascertain whether these reactions were encountered with compounds whose region of unsaturation was further removed from the alcohol or aldehyde group. In order to test this point the behavior of Δ^3,2,2-dimethylbutenol-1, $CH_2{=}CHC(CH_3)_2CH_2OH$, over alumina and zinc oxide was studied. The structure of this compound is such that the double linkage cannot migrate to the 2,3-position nor can it undergo dehydration to a diene.

The dimethylbutenol was passed over alumina and zinc oxide under the experimental conditions and with the results stated in Table I.

Table I

Reaction of Δ^3-2,2-Dimethylbutenol-1 over Aluminum and Zinc Oxides

			Rate per hour of passage of alcohol and formation of products				Gas analysis (%) (excluding N_2)				
	Catalyst	Temp. °C.	Alcohol, ml.	Aldehyde, moles	Hydrogen, moles	Gas, ml.	CO_2	CO	C_nH_{2n}	O_2	H_2
1	Alumina	300	19.3	0.030	0.0001	174	11.5	41.2	25.3	3.8	1.1
2	Zincoxide	300	20.5	.019	.0181	705	14.1	10.1	13.5	3.2	57.5
3	Zincoxide	330	19.4	.029	.0405	1652	8.1	18.0	18.3	2.0	55.0
4	Zinc oxide	330	16.0	.024	.0434	1360	3.5	19.9	7.0	...	71.5

The weight of aldehyde given in Expt. 4 was obtained by fractionation, while the amounts given in Expts. 1, 2 and 3 were obtained by weighing the amount of p-nitrophenylhydrazone formed as previously described. The same aldehyde, *i. e.*, A^3,2,2-dimethylbutenol-1, $CH_2{=}CHC(CH_3)_2$-CHO, was produced over both zinc and aluminum oxides, as was evidenced

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[1] Weston and Adkins, This Journal, 50, 1930 (1928); 51, 2430 (1929).

by the melting points of mixtures of the semicarbazones of the product from different experiments. There was also produced over both catalysts an unsaturated hydrocarbon boiling at **37–39'.** This hydrocarbon was apparently 3,3-dimethylbutene-1.

The behavior of the dimethylbutenol differed over the two catalysts in that practically no hydrogen was produced over alumina, while over zinc oxide there was a considerable amount of dehydrogenation.

It is obvious from the above facts that over alumiria, aldehyde was produced only through the autosxidation–reduction of the unsaturated alcohol (Equation III) while over zinc oxide this reaction occurred along with the dehydrogenation reaction (Equation IV) common to primary and secondary alcohols.

$$2CH_2{=}CHC(CH_3)_2CH_2OH = CH_2{=}CHC(CH_3)_2CHO + CH_2{=}CHC(CH_3)_2CH_3 \quad (III)$$

$$CH_2{=}CHC(CH_3)_2CH_2OH = CH_2{=}CHC(CH_3)_2CHO + H_2 \quad (IV)$$

This is in marked contrast to the behavior of allyl alcohol over zinc oxide which results in only a small amount of dehydrogenation but in the formation of large amounts of propionaldehyde according to reactions V and VI.

$$CH_2{=}CHCH_2OH = CH_2{=}CHCHO + H_2 \quad (V)$$

$$CH_2{=}CHCHO + CH_2{=}CHCH_2OH = CH_3CH_2CHO + CH_2{=}CHCHO \quad (VI)$$

Benzyl alcohol is similar to Δ^3,2,2-dimethylbutenol-1 in that it is a primary alcohol without a hydrogen atom on the 2-carbon atom and with unsaturation in the 3,4-position. When passed over alumina it behaved similarly to the dimethylbutenol in that disproportionation took place with the formation of benzaldehyde and toluene as in Equation VII. The experimental details are given in Table II.

$$2C_6H_5CH_2OH = C_6H_5CH_3 + C_6H_5CHO + H_2O \quad (VII)$$

$$C_6H_5CH_2OCH_2C_6H_5 = C_6H_5CH_3 + C_6H_5CHO \quad (VIII)$$

TABLE II

REACTIONS OF BENZYL ALCOHOL AND OF DIBENZYL ETHER OVER ALUMINA

Substance	Temp., °C.	Ml./hr.	Toluene per hour, g.	Dibenzyl ether, %	Toluene, %	Benzaldehyde, %
Dibenzyl ether	340	22.5	2.93	..	27.0	25.8
Benzyl alcohol	340	21.8	3.15	22.0	32.6	27.6
Benzyl alcohol	340	16.6	2.20	24.0	31.0	31.0
Benzyl alcohol	340	13.5	2.10	25.6	35.0	38.0

It is possible that the auto-oxidation reduction of benzyl alcohol involves the disproportionation of dibenzyl ether formed through the catalytic action of alumina on benzyl alcohol (Equation VIII) as dibenzyl ether is formed in a good yield when benzyl alcohol is passed over alumina. Toluene and benzaldehyde are formed in similar amounts irrespective of whether the alcohol or the ether is passed over the catalyst. It is reported that dibenzyl ether disproportionates under the influence of high temperatures but under the experimental conditions used in this investigation the amount of disproportionation of the ether was shown to be quite negligible except in contact with alumina.

The catalytic dehydration of a hydroxy ester over alumina is apparently accompanied by a considerable amount of disproportionation and rupture of the molecule. When the ethyl ester of β-hydroxybutyric acid was passed over alumina the dehydration (Equation IX) was accompanied by an almost equal amount of disproportionation (equation X).

$$CH_3CHOHCH_2COOC_2H_5 = CH_3CH{=}CHCOOC_2H_5 + H_2O \qquad (IX)$$
$$CH_3CHOHCH_2COOC_2H_5 = CH_3CHO + CH_3COOC_2H_5 \qquad (X)$$

A summary of the experimental results is given in Table III.

TABLE III

REACTION OF ETHYL β-HYDROXYBUTYRATE OVER ALUMINA

Temperature	325°	325"	325"	350°
Rate of passage of hydroxy ester, ml./hr.	10	17.7	26	20
Percentage split to acetaldehyde and ethyl acetate	26.4	24.2	19.2	29.3
Ethylcrotonate, %	35.2	32.6	26.2	33.3
Recovered ethyl β-hydroxybutyrate, %	25.4	33.4	45.5	22.0

The disproportionation of the hydroxy ester is not a reaction of ethyl crotonate, for that ester is quite stable over alumina at 325'. A reaction takes place exclusively in the sense of Equation X if the α,α-dimethyl-β-hydroxy ester is used. The yield of ethyl isobutyrate was 35.7% when 15.5 ml. of the hydroxy ester was passed over 2.5 g. of alumina at 325° for one hour. Ethyl 2-methyl-2-ethyl-3-hydroxybutyrate also reacts over alumina in the sense of Equation X. The yield of ethyl 2-methylbutyrate was 61% when 12.5 g. of the hydroxy ester was passed over 2.5 g. of alumina at 315° for one hour.

It has been shown that alumina catalyzes several types of reactions in hydroxy compounds: (1) dehydration of alcohols to ethers; (2) dehydration of alcohols and hydroxy esters to alkenes or unsaturated esters; (3) reduction of 2,3-unsaturated aldehydes and oxidation of alcohols; (4) intramolecular rearrangement of hydrogen in 2,3-unsaturated alcohols; (5) disproportionation without rupture of the molecule of alcohols having no hydrogen on the carbon atom alpha to the carbinol group; (6) disproportionation with rupture of the molecule of the ether of an alcohol of the type noted above; (7) disproportionation with rupture of the molecule of hydroxy esters, especially if there are substituents on the carbon adjacent to the carbinol group.

It is clear from a consideration of the diversity of the reactions noted above that it is a mistake to describe alumina as a dehydrating catalyst, for this characterization rests upon the chance that chemists first and most conveniently tested its activity toward simple saturated alcohols. The fact that water is split out of these simple alcohols should not therefore be allowed to bulk very large in devising an hypothesis to account for the catalytic activity of the oxide. Since the type of reaction induced varies with the space relationships in the organic molecule, it is reasonable to suppose that space relationships or the surface of different catalysts are factors in the type of reaction catalyzed. For the present it seems unwise to *go* beyond the conception that alumina activates or labilizes the organic molecule (and in the case of bimolecular reaction, orients molecules in juxtaposition) so that any one of several reactions is possible. The reaction actually resulting then depends upon the chemical and physical characteristics of the organic molecule.

Experimental Part

The data given under Expts. 1, 2 and **3** in Table I were obtained as described in a previous paper.' Two ml. of catalyst was used in studying the reactions of the alcohols and ethers while 2.5 ml. was used for the esters. Two and three-tenths grams of an unsaturated hydrocarbon boiling at 38–40° was fractionated out of the condensate from the passage of 15.5 g. of the dimethylbutenol over alumina at 300'. Five grams of the unsaturated hydrocarbon was obtained in three hours forty-four minutes (Expt. 4, Table I) from the alcohol over zinc oxide at 330°. On drying and redistillation it boiled at 37–39°. In all probability it is 3,3-dimethylbutene-1. Formin and Lochanski reported this hexylene to boil at 41.2' at 760 mm.[2] It was converted to the dibromide derivative, which boiled at 57–57.5° at 17 mm.; however, the quantities were too small to purify for a proper analysis. The yield of aldehyde in Expt. 4 was 9 g. and on redistillation and drying it boiled at 98.5 to 99.5'; d_{25}^{25} 0.8184; n_D 1.4072 at 25°. *Molecular refraction.* Calcd. for 2,2-dimethyl-Δ^3-butenal: 29.45. Found: 29.51. The aldehyde was converted to the semicarbazone derivative, which after two recrystallizations melted at 158.5–160.5" and was not changed by a third recrystallization.

Anal. Calcd. for $C_7H_{13}ON_3$: C, 54.19; H, 8.39. Found: C, 53.88, 53.97; H, 8.57, 8.55.

It was demonstrated that the aldehyde produced over alumina was identical with the aldehyde produced over zinc oxide by a mixed melting point of the semicarbazone derivatives, which was 158.5–160°. The melting point was 157.5–159° for the derivative of the aldehyde produced by alumina.

The toluene and benzaldehyde (Table II) from benzyl alcohol and dibenzyl ether were characterized by the formation of 2,4-dinitrotoluene and the phenylhydrazone of benzaldehyde. The percentage split to ethyl acetate and acetaldehyde (Table III) was determined by saponifying the 25 to 95° fraction of the condensate and titrating the acetic acid formed. The percentages of ethyl crotonate and percentages of recovered ethyl β-hydroxybutyrate were calculated from the results of the fractionation of the condensate. The acetaldehyde was characterized by the p-nitrophenylhydrazone, and the acetic acid by the *p*-toluidide.

The preparation of Δ^3,2,2-dimethylbutenol-1 is described in the preceding paper.[3]

Ethyl 2-methyl-2-ethyl-3-hydroxybutyrate was obtained by the reduction of ethyl a-methyl-a-ethylacetoacetate with a nickel catalyst in 87% yield;[4] b. p. 97–98' at 14.5 mm.; d_{25}^{25} 0.9775; n_D 1.4340 at 25°. Molecular *Refraction.* Calcd., 46.94. Found, 46.39.

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[2] Formin and Lochanski, *Ber.,* 46,244,1219 (1913).

[3] Folkers and Adkins, THIS JOURNAL, 53,1416 (1931).

[4] Adkins, Connor and Cramer, *ibid.*, ***52,*** 5195 (1930).

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.02; H, 10.42. Found: *C*, 61.64. 61.49. H, 10.42, 10.40.

Ethyl **2,2-dimethyl-3-hydroxybutyrate** was obtained by the reduction with a nickel catalyst of ethyl dimethylacetoacetate. Yields of 87–88% of the product were obtained which boiled from 94–95° at 21 mm.[4]

Ethyl **Δ^3,2,2-dimethylbutyrate** was obtained by the dehydration of ethyl 2,2-dimethyl-3-hydroxybutyrate with phosphorus pentoxide: b. p. 139–141°; yields, 74–80%.[5]

Catalysts.—Two hundred grams of aluminum nitrate was dissolved in two liters of cold water and concentrated ammonium hydroxide added with stirring until slightly ammoniacal. The precipitate was then filtered with suction and added to two liters of water, and stirred well to dissolve any soluble salt. The precipitate was filtered and added to one liter of water and well stirred again. After filtration the precipitate was dried in an oven at 125'. The alumina was then pulverized in a mortar and again placed in the oven until thoroughly dry. While it was still hot from the oven it was plunged into one liter of water. At this point some was lost due to the alumina forming a non-filterable suspension. After filtration, the oven drying at 125° was repeated. The dry powder was then pressed into pill form. This alumina had fair activity which was increased by heating at 400° for four hours. The zinc oxide was the same as that prepared by Weston from zinc oxalate.

Summary

Alumina does not catalyze (as with allyl alcohol) the reduction of the alkene linkage in Δ^3,2,2-dimethylbutenol-1 either through the rearrangement of hydrogen from the carbinol group of the same molecule or through the oxidation of a second molecule of the alcohol to an unsaturated aldehyde. Zinc oxide catalyzes the dehydrogenation of the alcohol to the aldehyde. Alumina and zinc oxide catalyze the autooxidation–reduction of Δ^3,2,2-dimethylbutenol-1 with the formation of an unsaturated aldehyde and unsaturated hydrocarbon. Benzyl alcohol and dibenzyl ether disproportionate in an analogous fashion. Alumina catalyzes the disproportionation of β-hydroxybutyric ester, and α,α-dialkyl-β-hydroxybutyric esters with the formation of acetaldehyde and a saturated ester.

MADISON, WISCONSIN

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[5] Courtot, *Bull. soc. chim.*, 35, 111–113 (1906).

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE HYDROGENATION OF CERTAIN BRANCHED COMPOUNDS OVER NICKEL

BY HOMER ADKINS, WALTER H. ZARTMAN AND HOWARD CRAMER

RECEIVED NOVEMBER 10, 1930 PUBLISHED APRIL 6, 1931

It has been generally recognized that the catalytic hydrogenation of substituted compounds is usually more difficult than in the case of the simpler compounds. Whether this apparent lowering in reactivity is due to spatial effects or otherwise is uncertain, but it seems worth while to study rather completely and carefully the hydrogenation of compounds which may be considered to fall into this group. Therefore the hydrogenations of triphenylcarbinol, triphenylmethane, dicyclohexylphenylmethane, 1,3,5-triphenylbenzene, triphenylamine, 1,3,5-trimethylbenzene and 2,2',4,4',6,6'-hexamethyldiphenyl have been investigated. The experimental methods and apparatus were essentially the same as those previously described.[1]

The significance for the present of most of the results reported in this paper lies in the establishment of experimental conditions under which these hydrogenations may be carried out, so that little need be written in addition to the tabulation. There is recorded in Table I a summary of the experimental conditions and results obtained in typical experiments in the hydrogenation of the above list of compounds. There are reported: (1) the name of the compound, (2) the amount submitted to hydrogenation, (3) the amount of hydrogen absorbed, (4) in the time and (5) at the temperature, (6) and pressure, (7) over the catalyst, (8) and in the amount of solvent indicated; (9) the yield(s) of, (10) product(s) having, (11) the physical constants compared with, (12) the physical constants, (13) previously reported.

The most noteworthy observation made in connection with the hydrogenation of these compounds was that water or ethanol inhibited the reduction of the benzenoid ring in dicyclohexylphenylmethane, while they were without effect upon the hydrogenation of two of the benzenoid rings in triphenylmethane. Dicyclohexylphenylmethane was formed quantitatively by the hydrogenation of triphenylcarbinol in alcohol or methylcyclohexane, and of triphenylmethane in alcohol or in methylcyclohexane containing water. Dicyclohexylphenylmethane in ethanol solution absorbed no hydrogen over an active nickel catalyst at 200° under a pressure of 100 atmospheres of hydrogen.

Tricyclohexylmethane was readily formed by the hydrogenation in methylcyclohexane of triphenylmethane or dicyclohexylphenylmethane.

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[1] Adkins and Cramer, THIS JOURNAL, 52, 4349 (1930).

TABLE I

HYDROGENATION OF VARIOUS COMPOUNDS OVER NICKEL

Compound		Moles H_2	Time, hrs.	Temp., °C.	Pressure, atm.	Catalyst, g.	Solvent, ml.	Yields	Product	Physical constants	
Name	Moles									Found, °C.	Reported, °C.
Triphenylmethane	0.10	0.99	2	175	106 ±17	3 Z 8	C_7H_{14} 50	A90 B100	Tricyclohexylmethane	M. p. 58.5–59.5	M. p. 48;[a] b. p. 340–345[b]
Triphenylmethane	.10	.97	6.5	200	110 ±15	3 Z 5	C_7H_{14} 75	A88 B100	Tricyclohexylmethane	164–165 (3 mm.)	140 (20 mm.)[c]
Triphenylmethane	.10	.61	9	200	122 ±20	3 Z 8	C_2H_5OH 75	A78 B100	Dicyclohexylphenylmethane	161–163 (2 mm.)	196–197 (17 mm.)[a]
Triphenylmethane	.10	.62	9	200	123 ±21	3 Z 8	C_7H_{14} 50 + H_2O, 1.8 g.	A92 B100	Dicyclohexylphenylmethane	169–171 (3 mm.)	210–212 (20 mm.)[c]
Triphenylcarbinol	.10	.83	9	200	106 ±15	3 Z 8	C_7H_{14} 50	A87 B100	Dicyclohexylphenylmethane	169–171 (3 mm.)	
Triphenylcarbinol	.10	.80	12	200	110 ±16	3 Z 8	C_2H_5OH 75	A90 B100	Dicyclohexylphenylmethane	166–170 (3 mm.)	
Dicyclohexylphenylmethane	.10	.35	6	200	101 ±13	3 Z 8	C_7H_{14} 50	A91 B100	Tricyclohexylmethane	M. p. 58.5–59.5	
Triphenylamine	.05		2.5	200	106 ±22	3 Z 8	C_7H_{14} 50	A65 B100	Tricyclohexylamine	M. p. 160–161	170–171 (4 mm.)[d]
Triphenylamine	.11	1.00	6	175	220 ±40	2 H. C. 12	C_7H_{14} 75	A96	Tricyclohexylamine	188–189 (7 mm.)	
Mesitylene	.50	1.61	6	200	110 ±35	3 Z 7	None	A90 B100	1,3,5-Trimethylcyclohexane	136–138 (740 mm.)	135.5–136 (743 mm.)[e]
Mesitylene	.50	1.60	4	200	108 ±40	3 Z 7	None	A92 B100	1,3,5-Trimethylcyclohexane	136–138 (740 mm.)	136–140 (760 mm.)[f]
1,3,5-Triphenylbenzene	.10	1.16	12	200	106 ±17	3 Z 8	C_7H_{14} 75	A94 B100	1,3,5-Tricyclohexylcyclohexane	M. p. 159–160	
1,3,5-Triphenylbenzene	.10	1.12	12	200	98 ±9	3 Z 5	C_7H_{14} 75	A86 B100	1,3,5-Tricyclohexylcyclohexane	228–228.5 (3.5 mm.)	
Dimesityl	.10	0.60	18	200	124 ±23	3 Z 8	C_7H_{14} 75	A90 B100	2,2′,4,4′,6,6′-Hexamethyldicyclohexyl	123–126 (3 mm.)	

[a] Ipatiev and Dolgov, *Compt. rend.*, **185**, 210 (1927); **183**, 304 (1925). [b] Zelinski and Goverdovskaia, *Ber.*, **60B**, 713 (1927); [c] Godchot, *Compt. rend.*, **147**, 1057 (1909). [d] Adams and Hiers, THIS JOURNAL, **49**, 1099 (1927); [e] Adams and Marshall, *ibid.*, **50**, 1970 (1928). [f] J. Klepper, *Chem. Ind.*, Spec. No. 261 (February, 1929) [*Chem. Abstracts*, **23**, 3897 (1929)].

It was found to be a white crystalline substance melting at 58.5–59.5° rather than a liquid as reported by Zelinski and Goverdovskaia and by Godchot or a solid melting at 48° as observed by Ipatiev and Dolgov.

Tricyclohexylamine was found to be a solid melting at 160–161°. Both the absorption of hydrogen in its formation and the analysis of the product indicated quite definitely that the three phenyl groups in triphenylamine had been converted to cyclohexyl groups. Adams and Hiers obtained a liquid as the result of the hydrogenation of triphenylamine over platinum which they reported on the basis of its nitrogen content as being tricyclohexylamine. Their results have been duplicated in this Laboratory but it is believed that the product is not pure tricyclohexylamine. Analyses for carbon and hydrogen on this material were about 2% from the theoretical values. Analyses for nitrogen are not significant in this case because the presence of rather considerable percentages of impurities such as dicyclohexylphenylamine do not greatly modify the nitrogen content.

Symmetrical tricyclohexylcyclohexane and hexamethyldicyclohexyl have been prepared for the first time.

Experimental Part

Triphenylcarhinol (m. p. 162–162.5°), triphenylmethane (m. p. 92–93°), triphenylamine (m. p. 126–126.5°) and mesitylene (1,3,5-trimethylbenzene) (b. p. 163.5–164.5") were prepared by standard methods. 2,2′,4,4′,6,6′-Hexamethyldiphenyl (dimesityl) (m. p. 100–100.5°) and the intermediate bromomesitylene were prepared *as* by Adams and Moyer, and by Smith and MacDougall.[2] The 1,3,5-triphenylbenzene (m. p. 172–173") was prepared as by Fischer, Wille and Vorländer.[3] Dicyclohexylphenylmethane was prepared by the hydrogenation, as indicated in Table I, of triphenylcarbinol or of triphenylmethane. Both mesitylene and dimesityl were refluxed for many hours over sodium for the removal of traces of halogen-containing compounds. Dimesityl was further treated five times for three or four hours with reduced nickel (no support) in methylcyclohexane at 200° under 100 atmospheres.

The catalysts referred to as H. C. 12, and Z 5 were made as by Cramer. Catalysts Z 7 and 8 were made similarly except that sodium bicarbonate was used as the precipitant for nickel. Catalysts 7 and 8 were different preparations in which the same method was used.

Properties and Analyses of Products.—Tricyclohexylmethane. *Anal.* Calcd. for $C_{19}H_{34}$: C, 86.93; H, 13.07. Found: C, 86.50, 86.74; H, 13.23, 13.53. Dicyclohexylphenylmethane. *Anal.* Calcd. for $C_{19}H_{26}$: C, 88.98; H, 11.02. Found: C, 88.65, 88.65; H, 11.24, 11.05; $d^{25°}_{25°}$ 0.9724; n^{25}_{D} 1.5372; MR'_{D}, calcd. 82.07; found, 82.32. 1,3,5-Tricyclohexylcyclohexane. *Anal.* Calcd. for $C_{24}H_{42}$: C, 87.18; H, 12.82. Found: C, 36.86, 86.94; H, 12.90, 12.84. 2,2′,4,4′,6,6′-Hexamethyldicyclohexyl. *Anal.* Calcd. for $C_{18}H_{34}$: C, 86.31; H, 13.69. Found: C, 86.45, 86.57; H, 13.83, 13.75; d^{25}_{25} 0.8932; n^{25}_{D} 1.4873; MR'_{D}, calcd. 80.75; found, 80.62. Tricyclohexylamine. *Anal.* Calcd. for $C_{18}H_{33}N$: C, 82.04; H, 12.64. Found: C, 82.12, 82.29, 82.32; H, 12.63, 12.68, 12.61. Neutral equivalent. Calcd. 263. Found: 265. Hydrobromide

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[2] Adams and Moyer, THIS JOURNAL, 51, 630 (1929); Smith and MacDougall, *ibid.*, 51, 3002 (1929).

[3] Fischer, Wille and Vorlander, *Ber.*, 62, 2836 (1929).

of tricyclohexylamine (m. p. 267–268°). *Anal.* Calcd. for $C_{18}H_{34}NBr$: Br, **23.21.** Found: Br, **23.15.** Hydrochloride of tricyclohexylamine (m. p. 264°). *Anal.* Calcd. for $C_{18}H_{34}NCl$: Cl, **11.63.** Found: Cl, **11.89.** Picrate of tricyclohexylamine (m. p. 172.5–173°). "Tricyclohexylamine" from hydrogenation over platinum, b. p. 171–173° (4 mm.). *Anal.* Calcd. for $C_{18}H_{33}N$: C, **82.04;** H, **12.64.** Found: C, **84.48, 84.27;** H, **10.69, 10.62.**

Summary

Experimental conditions for the successful hydrogenation over nickel of triphenylcarbinol, triphenylmethane, dicyclohexylphenylmethane, 1,3,5-triphenylbenzene, triphenylamine, 1,3,5-trimethylbenzene and 2,2′,4,4′-6,6′-hexamethyldiphenyl have been determined. Water and ethanol have been found to inhibit the hydrogenation of dicyclohexylphenylmethane. 1,3,5-Tricyclohexylcyclohexane and 2,2′4,4′,6,6′-hexamethyldicyclohexyl have been prepared for the first time. Tricyclohexylmethane and tricyclohexylamine have been found to have physical properties very different from those previously reported.

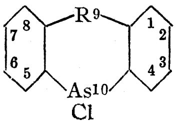
MADISON, WISCONSIN

DERIVATIVES OF THE ARSENIC ANALOG OF 9,10-DIHYDROACRIDINE. I[1]

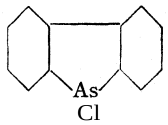
BY WILLIAM GUMP AND HUGO STOLTZENBERG

RECEIVED NOVEMBER 25, 1930 PUBLISHED APRIL 6, 1931

Compounds of the type represented by the Formula I are known in which R is: NH, (10-chloro-9,10-dihydrophenarsazine);[2] 0, (10-chloro-9,10-dihydrophenoxarsine);[3] S, (10-chloro-9,10-dihydrophenthiarsine);[4] AsCl, (9,10-dichloro-9,10-dihydroarsanthrene).[5] This series contains the arsenic as a hetero atom in a six-membered ring; an example of a five-membered ring is the *o,o′*-diphenylylene arsenious chloride (II).[6]



I



II

The synthesis of these compounds can be accomplished in the cases of R=NH and O by heating arsenic trichloride with diphenylamine and with diphenyl ether, but this reaction does not take place with diphenyl,

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[1] Read before the Division of Organic Chemistry at the **77th** meeting of the American Chemical Society, Columbus, Ohio, April **29** to May **3, 1929.**

[2] Bayer and Co., German Patent **281,049 (1913);** Wieland and Rheinheimer, *Ann.* **439, 1 (1921).**

[3] Lewis, Lowry and Bergeim, THIS JOURNAL, **43,891 (1921);** Turner and Sheppard, *J. Chem. Soc.*, **127,544 (1925).**

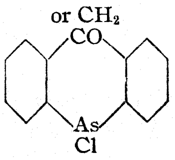
[4] Roberts and Turner, *ibid.*, **129,1207 (1926).**

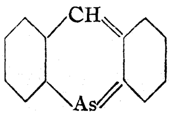
[5] Kalb, *Ann.*, **423, 39 (1921).**

[6] Aeschlimann and co-workers, *J. Chem. Soc.*, **127, 66 (1935).**

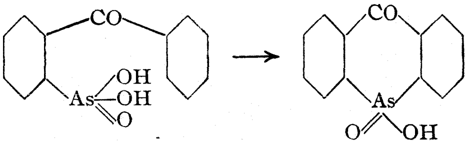
diphenylsulfide, diphenylmethane or benzophenone, and other methods have to be used to synthesize these arsenical ring compounds.

Analogs of acridone, 9,10-dihydroacridine and acridine where the nitrogen is replaced by arsenic and which have the structure shown by the Formulas III and IV, thus belonging to the general type I, have not yet been prepared although several attempts have been made to secure such compounds.

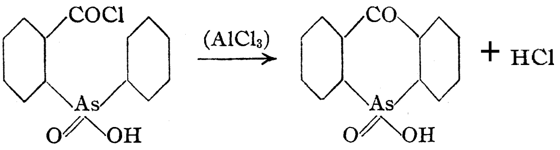

III


IV

Aeschlimann and McCleland[7] had studied the synthesis of the acridone analog (III) by different methods. They tried to close the ring from benzophenone-o-arsonic acid by removing the elements of water by means of sulfuric acid or phosphorus pentoxide in the same way that anthraquinone is prepared from o-benzoylbenzoic acid. This method was used successfully in some syntheses of arsenic ring compounds, but the ring formation did not occur here.



Another way was to start from o-carboxydiphenylarsinic acid. Aeschlimann prepared the acid chloride and tried to split off hydrogen chloride by means of aluminum chloride in order to close the ring, but the desired compound could not be obtained. Sakellarios[8] was also unsuccessful in his attempts to form the ring from the o-carboxydiphenylarsinic acid, using water-removing condensation agents.



The work done already showed that the synthesis of an arsenic acridone analog is a difficult task. The object of our research was to see if the CH_2 group instead of the CO group would make the ring formation easier and would give the possibility of obtaining acridine and acridone rings with arsenic instead of nitrogen. We propose the name acridarsine for this new

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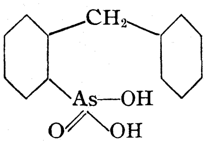
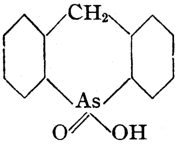
[7] Aeschlimann and McCleland, *J. Chem. Soc.*, 125,2025 (1924).

[8] Sakellarios, *Ber.*, 59, 2552 (1926).

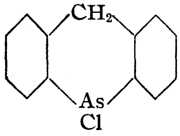
series. We were able to prepare the acridarsinic acid (VI) and the 10-chloro-9,10-dihydroacridarsine (VII).



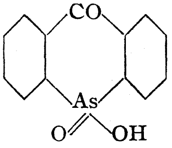
V



VI



VII

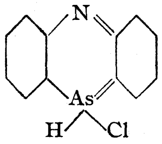


VIII

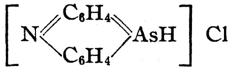
The first step was the preparation of diphenylmethane-*o*-arsonic acid (V) from o-aminodiphenylmethane. The well-known method of Bart was used; the diazo solution of o-aminodiphenylmethane was coupled with sodium arsenite to the diphenylmethane-o-arsonic acid. This arsonic acid could be closed to a ring by means of concentrated sulfuric acid without difficulty, in contrast to the benzophenone-o-arsonic acid. Acridarsinic acid (VI) was so formed.

The acridarsinic acid was then reduced to the 10-chloro-9,10-dihydroacridarsine (VII) by means of sulfur dioxide and hydrochloric acid. This compound forms beautiful, yellow-greenish prisms and has distinct physiological properties. It shows the disagreeable qualities of acridine in an increased degree. When dusted in the air in smallest amounts, it causes severe burning of the face, the lips and the tongue. In addition to that, the trivalent arsenic strongly irritates the mucuous surfaces of the bronchial organs in the same way as 10-chloro-9,10-dihydrophenarsazine and other organic arsenic compounds.

In a recent publication, Kappelmeier[9] suggested a new formula for 10-chloro-9,10-dihydrophenarsazine by reason of his experimental results, namely

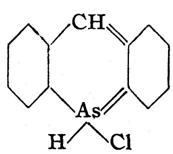


or



$\left[\mathrm{N}\begin{array}{c}\diagup\mathrm{C_6H_4}\diagdown\\ \diagdown\mathrm{C_6H_4}\diagup\end{array}\mathrm{AsH}\right]\mathrm{Cl}$

As the 10-chloro-9,10-dihydroacridarsine behaves like acridine in its skin-irritating properties, it may be also an arsonium salt and have a figuration which is derived from acridine and not from 9,10-dihydroacridine.



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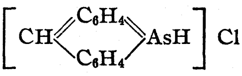

$\left[\mathrm{CH}\begin{array}{c}\diagup\mathrm{C_6H_4}\diagdown\\ \diagdown\mathrm{C_6H_4}\diagup\end{array}\mathrm{AsH}\right]\mathrm{Cl}$

The preparation of the acridine analog (III) from the 10-chloro- or the 10-methoxy-9,10-dihydroacridarsine will be investigated.

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[9] Kappelmeier, *Rec. trav. chim.*, **49**, 64 (1930).

Another reaction which will be studied is the oxidation of acridarsinic acid. By means of chromic acid–sulfuric acid mixture a new acid, melting above 260°, was obtained from acridarsinic acid. This is probably the 9-oxo-acridarsinic acid (VIII) and the oxidation would lead to the compounds which Aeschlimann was not able to synthesize.

Experimental Part

***o*-Aminodiphenylmethane.**—The preparation of this starting material is quite troublesome. Commercial o-nitrotoluene was chlorinated to o-nitrobenzyl chloride according to the method of Haussermann and Beck[10] using sulfur as chlorine transporter. The yield was always low and could not materially be increased by exposing the reaction mixture to sun or artificial light. For future experiments, it may be more advantageous to nitrate benzyl chloride and to separate the o- and *p*-nitrobenzyl chlorides.

The o-nitrobenzyl chloride, benzene and aluminum chloride resulted in *o*-nitrodiphenylmethane in a yield of about *75%;* the method of Geigy and Königs,[11] modified by Tanasescu,[12] was applied.

o-Nitrodiphenylmethane was reduced to the amino compound with tin and hydrochloric acid. Fischer and Schütte[13] claim that the reduction proceeds very slowly; we found, however, that *50* g. of nitrodiphenylmethane was reduced completely in about one hour. The yield of pure o-amino diphenylmethane is at least 80%.

The alkaline reduction of o-nitrodiphenylmethane, described by Carre,[14] did not give satisfactory results.

Diphenylmethane-*o*-arsonic Acid.—Thirty-seven grams of *o*-aminodiphenylmethane was dissolved in about *100* cc. of ether. The ether solution was allowed to drop with stirring upon a mixture of *70* cc. of hydrochloric acid and *700* g. of finely crushed ice. The separated hydrochloride was brought into solution by diazotizing with $N/10$ sodium nitrite solution.

Forty grams of arsenious oxide was dissolved in *120* cc. of *5* N sodium hydroxide and *300* cc. of sodium carbonate solution *(106* g. of anhydrous sodium carbonate in a liter of solution), *25* cc. of an ammoniacal solution of copper sulfate (1:10) and *600* cc. of water were added. This mixture and the diazonium solution were dropped onto *500* g. of ice under stirring during one hour. On the next morning the tar was filtered off, the boiling liquor was decolorized with Darco or Nuchar and hydrochloric acid was added until the solution was neutral. The small amounts of a by-product were filtered off, and the arsonic acid *(16* g.) was precipitated by the further addition of hydrochloric acid until congo paper showed blue color.

The diphenylmethane-o-arsonic acid is obtained in beautiful, white needles by recrystallization from a large amount of water. The acid, melting at 161–162°, is very slightly soluble in cold water, and somewhat soluble in boiling water. Glacial acetic acid is a good solvent for the arsonic acid.

Anal. Subs., *0.2034:* $Mg_2As_2O_7$, *0.1070.* Calcd. for $C_{13}H_{13}O_3As$: As, *25.7.* Found: As, *25.4.*

Acridarsinic Acid.—Ten grams of diphenylmethane-o-arsonic acid was dissolved in *40* cc. of concentrated sulfuric acid; the solution was heated in boiling water for five

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[10] Haussermann and Beck, Ber., *25,2445 (1892).*

[11] Geigy and Konigs, *ibid.*, 18, 2402 *(1885).*

[12] Tanasescu, Bull. *soc. chim.*, [4] **39,** *1453 (1926).*

[13] Fischer and Schiitte, Ber., *26, 3086 (1893).*

[14] Carre, Bull. *soc.* chim., [4] *5,119 (1909).*

minutes, and poured into about 500 cc. of water. Glittering, colorless crystals separated which were filtered and washed with water. The yield is almost quantitative. The crystals melt at 230–235°, becoming yellow at 200° and brown shortly before melting. The acid is obtained in small needles by recrystallization from dilute acetic acid, which melt at 235–236° with disintegration. The acridarsinic acid is almost insoluble in cold and also in boiling water; in warm glacial acetic acid, it is easily soluble.

Anal. Subs., 0.2026: $Mg_2As_2O_7$, 0.1164. Calcd. for $C_{13}H_{11}O_2As$: As, 27.5. Found: As, 27.7.

10-Chloro-9,10-dihydroacridarsine.—Ten grams of acridarsinic acid was finely pulverized and suspended in 100 cc. of hydrochloric acid; 100 cc. of chloroform was added to the suspension. By means of a wide tube which was submerged below the surface of the chloroform, sulfur dioxide and hydrogen chloride were passed through. After five minutes, a little potassium iodide was added and the reduction was completed on the steam-bath under refluxing.

The chloroform solution was separated from the aqueous liquor and the chloroform was distilled off on the steam-bath. The 10-chloro-9.10-dihydroacridarsine (9 g.) remained in large crystals of brownish color. The substance was obtained in beautiful, yellow prisms by recrystallization from benzene. The 10-chloro-9,10-dihydroacridarsine is soluble in the common organic solvents and melts at 114–115°.

Anal. Subs., 0.1411: $Mg_2As_2O_7$, 0.0778. Subs., 0.2318: AgCl, 0.1200. Calcd. for $C_{13}H_{10}ClAs$: As, 27.1; Cl, 12.83. Found: As, 26.7; Cl, 12.81.

Summary

Starting with o-aminodiphenylmethane, the diphenylmethane-o-arsonic acid and derivatives of the arsenic analog of 9,10-dihydroacridine, such as acridarsinic acid and 10-chloro-9,10-dihydroacridarsine have been synthesized.

BINGHAMTON, NEW YORK

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

THE PIRIA REACTION. I. THE OVER-ALL REACTION[1]

BY W. H. HUNTER AND MURRAY M. SPRUNG

RECEIVED NOVEMBER 28, 1930 PUBLISHED APRIL 6, 1931

Aminosulfonic acids can be obtained directly from aromatic nitro compounds by heating the latter with metal sulfites and then boiling with mineral acids. This reaction was discovered by Piria[2] in 1851, and will therefore be referred to in the following pages as "the Piria reaction." Piria, at that time, subjected α-nitronaphthalene to the action of ammonium sulfite in dilute alcoholic solution, and isolated two reduction products: the ammonium salts of naphthionic acid and of α-naphthylsulfaminic acid, respectively.

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[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1928. Presented before the Division of Organic Chemistry of the American Chemical Society at the Minneapolis Meeting, September 9–16, 1929.

[2] Piria, *Ann.*, 78, 31 (1851).

It would naturally be expected that this reaction would be of importance in the manufacture of intermediates for azo dyes and some such hope undoubtedly has inspired many workers, for in the eighty years which have intervened since its discovery, the Piria reaction has been studied by a large number of investigators.[3]

However, the information which has been obtained has been of a decidedly general nature. No systematic investigation, from a theoretical point of view, of a series of nitro compounds has been carried out; no two investigators have used identical procedures for carrying out the reduction, or for isolating the products. The original ammonium sulfite has in many cases been replaced by sodium or potassium sulfite of various concentrations, or by equally varied concentrations of bisulfite. Also, much of the information is in the usual none too clear specifications of *an* organic chemical patent of the early days.

Further, with the exception of Raschig,[4] no one has given any particular consideration to the mechanism of the changes involved.

Now the Piria reaction is carried out in two distinct stages: a reduction stage, in which the nitro group is known to be transformed into an amino group, a sulfaminic acid group, or both; and an acid treatment stage, in which an amine or an aminosulfonic acid appears. It is entirely fair, it would seem, to say that neither of these stages is understood, though many opinions have been expressed about both of them taken singly and together.

This situation is due primarily to the fact that most previous investigators other than Raschig, and perhaps Weil,[5] have been primarily interested in finding the best reagent and the best conditions for the production of a single desired compound, usually an aminosulfonic acid.

Aside from its value, or lack of it, as *a* source of intermediates, the

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[3] The most important published articles and a number of the more significant patent citations are as follows: Hilkenkamp, Ann., 95, 86 (1855); Carius, *Z. Chem. Pharm.*, 632 (1861); Smit, *Ber.*, 8,1442 (1875); Nietzki, *ibid.*, 29,2448 (1896); German Patent 86,097, *Friedlander*, 4, 90 (1895); Walter, German Patent 109,487, *ibid.*, **5**, 70 (1899); Turner, German Patent 123,115, *ibid.*, 6,171 (1900); Weil, German Patents 147,552 and 151,134, *ibid.*, 7, 58 and 61 (1902); Weil and Moser, *Ber.*, 55, 732 (1922); Weil and Wassermann, *ibid.*, 55, 2533 (1922); E. and H. Erdmann, German Patent 65,240, ***Friedländer***, **3**, 41 (1891); Willgerodt, *J. prakt. Chem.*, 32, 117 (1885); Meister, Lucius and Briining, German Patents, 92,082 and 215,338, ***Friedländer***, 4, 528 (1895), and 10, 182 (1910); Alfred Fischesser and Company, German Patent 79,577, ***ibid.***, 4, 565 (1894); Bayer and Company, German Patent 113,944, *ibid.*, 6, 184 (1900); Bucherer and Borsch, J. *prakt. Chem.*, [2]111,329 (1925); Meister, Lucius and Briining, German Patents 78,772 and 126,804, *Friedlander*, 4, 305 (1894) and 6, 384 (1901); Bayer and Company, German Patent 103,395, *ibid.*, 5,252 (1897); Raschig, "Stickstoff and Schwefel Studien," Verlag Chemie G. m. b. H., Leipzig, 1924.

[4] Raschig, "Stickstoff and Schwefel Studien," Verlag Chemie G. m. b. H., Leipzig, 1924, pp. 254-272.

[5] Weil and Wassermann, *Ber.*, 55, 2533 (1922), and earlier references cited therein.

reaction presents interesting problems, as a study in oxidation–reduction, and as a problem in the effect of hydrogen-ion concentration.

However, the methods of carrying out the reaction have been so various that it was impossible to gain a viewpoint on previous work. It therefore seemed wise to set up certain standard conditions, into which any nitro compound would be forcibly fitted, both for the reduction stage and the acid-treatment stage, in order to arrive at some uniformity of treatment. This was done, and a series of eight somewhat coherently related nitro compounds was studied, under these standard conditions, as well as with some deliberate variation, in certain cases. In the discussion of this treatment it is convenient to use the terms "standard reduction," "standard acid treatment," and in addition, the term "over-all reaction," the latter referring to the use of both operations in sequence.[6]

The results of this preliminary survey of the reaction are set forth in the table. . It will be noted that the standard procedure is not indicated for two of the nitro compounds. In these cases the standard procedure was used, but it failed to give satisfactory reduction, and the actual procedures are included, to illustrate the possibilities of variation, and as examples of the types of variation to be found in existing literature.

Discussion of the Results

It will be noted that in every case the over-all reaction produced an aminosulfonic acid, and in every case but one (*p*-nitrophenol)[7] an amine

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[6] STANDARD REDUCTION.—To a weighed quantity of the nitro compound was added enough of a 5.2 N (2.6 M) solution of sodium bisulfite to constitute approximately 75% excess over that calculated on the basis of 3 moles of bisulfite per mole of nitro compound. Enough 5 normal sodium hydroxide was then added to neutralize one-fourth of the bisulfite, and to the whole was added water in the ratio of 1250 cc. for each mole of nitro compound. This mixture, contained in a round-bottomed flask, was heated to boiling under a reflux condenser (with continual mechanical stirring) until homogeneous. (At this time the odor of nitro compound should be no longer noticeable.)

STANDARD ACID TREATMENT.—The mixture was evaporated on the steam-bath to about half the original volume, and treated while hot with 250 cc. of concentrated (12 N) hydrochloric acid for each mole of original nitro compound. It was boiled for one-half to two hours, and then allowed to cool.

ISOLATION.—In all cases where the amine produced was volatile with steam, excess alkali was added at this point, and the amine distilled out in a current of steam. The sodium salt of the aminosulfonic acid usually crystallized from the cooled residue, since such sodium salts are quite insoluble in an alkaline salt solution of the concentration here produced. This method of isolating the products was varied whenever it was necessary or more convenient to use other means. The procedure was especially different in case of those reactions which gave rise to amines which are not volatile with steam. These reactions are described separately, as a general statement cannot be made about them.

[7] For reasons stated in the experimental part of the paper, we believe that very little, if any, amine was produced in this case.

TABLE I

NATURE AND QUANTITY OF PRODUCTS OBTAINED IN THE "OVER-ALL" PIRIA REACTION

Nitro compound	Experimental condition	Time for reduction phase, hours	Amine isolated	Av., %	Aminosulfonic acid isolated	Av., %	Other product isolated	Av., %
Nitrobenzene	St. proc.	1.25	Aniline	26	Sulfanilic	27	......	..
α-Nitronaphthalene	St. proc.	5	α-Naphthyl-	2	Naphthionic	25	1-Naphthylamine-2,4-disulfonic acid	66
o-Nitrotoluene	Same	12	*o*-Toluidine	40	2-Toluidine-5-sulfonic	34	Sodium *o*-tolylsulfaminate	12
p-Nitrotoluene	Same	5	*p*-Toluidine	72	4-Toluidine-3-sulfonic	11	......	..
Nitro-*p*-xylene	3 Times[a] usual amt. water	17	*p*-Xylidine	60	3-Amino-1,4-xylene-6-sulfonic	16	......	..
m-Dinitrobenzene	*A* 10% excess Na_2SO_3(HCl used[c])	2	*m*-Nitroaniline	Tr.	*A* *m*-Nitraniline *p*-sulfonic	64	......	..
	B 110% excess $NaHSO_3$(H_2SO_4 used)	8.5[b]	......	..	*B* *m*-Nitraniline *p*-sulfonic	1	*m*-Phenylenediamine-*p*-sulfonic acid	10
p-Nitrobenzoic acid	St. proc.	4.5	*p*-Aminobenzoic acid	21[d]	*p*-Amino-*m*-sulfobenzoic	61[e]	......	..
p-Nitrophenol	St. proc.	11[f]	......	..	*p*-Aminophenol-*m*-sulfonic	14	......	..

[a] When the normal amount of water was used, the reaction was found to be incomplete even after twenty or twenty-five hours of boiling. [b] The reaction was not complete at this time. [c] The standard reduction gave an abnormal reaction. [d] Isolated partly as such, and partly as the *p*-amino-*m*-sulfobenzoic acid salt of *p*-aminobenzoic acid. [e] Isolated partly as such and partly as the *p*-amino-*m*-sulfobenzoic acid salt of *p*-aminobenzoic acid. [f] The reduction was probably complete, in this case, in a much shorter time than is here indicated. Since there was no external evidence indicating just when the reduction phase was ended (as there was in all other cases) the heating was continued until we were sure that no unreacted nitro compound remained.

could be obtained. However, the relative amounts of these products varied widely, indicating that their formation is very probably largely governed by constitution factors. This is probably the most striking result of the present work. Without presuming to be arbitrary, since the evidence available at present is still not very extensive, we may recognize several definite influences. Thus it is apparent that a ring methyl group favors the formation of amines, while the presence of a carboxyl group, a second nitro group, or a condensed ring favors the formation of aminosulfonic acids. In the few cases studied, the position of the second substituent seems to be of comparatively small influence.

In most cases, the combined yields of the two chief products (amine and mono-sulfonated amine) was slightly in excess of 80%. Only in two cases was it less. In the case of α-nitronaphthalene, the chief product was found to be an amino-disulfonic acid (isolated in 66% yield), and the total yield of this plus those of the two normal products was close to 95%. In the second case, that of nitrobenzene, we have not as yet succeeded in isolating a disulfonic acid. It is possible that the production of a very soluble disulfonic acid (extremely difficult to separate from the admixed inorganic salts) may account for the low total yield. We also believe it highly probably that in most of the other cases (that of *p*-nitrophenol is an exception, due to the inadequacy, in this case, of the methods used to isolate the product) the difference between the combined yields of the two chief products and 100% may be largely due to the occurrence of other very soluble amino-disulfonic acids, which we have not as yet attempted to isolate.

Another significant observation should be mentioned. It was noted that the speed of the first phase of the reaction (reduction) increased with dilution. This effect was particularly noted in experiments with nitrobenzene and with 2-nitro-1,4-xylene.[8] This led us to suspect that one of the early stages of the reaction is an *ionic* reduction, a suspicion which was lent further support by other observations. Thus it was noticed, in the case of α-nitronaphthalene, that the use of alcoholic aqueous media appreciably slowed down the reaction, contrary to expectation. It was also noted that neutral sodium sulfite was able to reduce dinitrobenzene in two hours, whereas bisulfite required over eight and one-half hours. All these observations can be reconciled with the view that for these reductions, the activity of the sulfite ion is of great importance.

On the contrary, however, it has been determined that partially neutralized sodium bisulfite is more effective in these reactions than normal

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[8] It should be mentioned that the velocity of the first phase of the reaction (usually a heterogeneous reaction) depended upon the efficiency of agitation. However, it was attempted to keep this factor as constant as possible, and the results recorded are therefore comparable.

sodium sulfite. At present we can harmonize this with the above observation relative to dinitrobenzene only by the assumption that another stage in the reduction is favored by higher hydrogen-ion concentration than is furnished by neutral sulfite, and that this factor, in the case of dinitrobenzene, is of secondary importance, for some reason which is not as yet clear. In this connection it should also be stated that the addition of alkali had little or no effect upon the speed of reduction of α-nitronaphthalene. Completely neutralized bisulfite and un-neutralized bisulfite, in this case, were about equally effective. We hope to throw more light upon these problems by virtue of further investigations now being carried out in this Laboratory.

Experimental Part

Experiments with a-Nitronaphthalene

(A) With Bisulfite and Aqueous Alcohol.—Twenty-five grams of α-nitronaphthalene (m. p. 57–57.5°), 76 cc. of 5.2 N sodium bisulfite (15% excess), 100 cc. of 95% alcohol, and 200 cc. of water were heated under a reflux condenser. At the boiling point of the solution the reduction was incomplete at the end of thirteen hours. By working up the mixture there was obtained 9.5 g. of naphthionic acid, 7 g. of a-nitronaphthalene (unchanged), and 0.8 g. of a-naphthylamine; yields (on the basis of the nitro compound used): amine, 10%; aminosulfonic acid, 58%.

(B) With Aqueous Bisulfite.—A typical run is given. Thirty-five grams (0.2 mole) of a-nitronaphthalene, 200 cc. of 5.2 N sodium bisulfite (75% excess) and 250 cc. of water were heated under a return condenser until the mixture was completely homogeneous. The contents of the flask, evaporated to 300 cc. and treated with 50 cc. of 12 N hydrochloric acid, gave a heavy white precipitate, which was filtered from the cooled solution. This mixture was warmed with 300 cc. of water, which dissolved the salts present, leaving the naphthionic acid (soly., 0.024 g. in 100 cc. of water); 13.5 g. (29%) of the aminosulfonic acid was thus obtained.

The combined filtrates were saturated with sodium chloride, and the precipitate produced was filtered off. It was nearly free from inorganic salts. When dry it weighed 31 g., which, on the basis of a monosodium salt of a naphthylamine disulfonic acid is equivalent to a yield of 66%.

(C) With Aqueous Bisulfite and Alkali.—Thirty-five grams was reduced according to the standard procedure. The reduction required five hours. Acidification with 50 cc. of 12 N hydrochloric acid gave 10 g. (22%) of naphthionic acid. Seventy-five grams of stick sodium hydroxide was added to the combined filtrates and steam passed through, giving 0.5 g. or 2% of α-naphthylamine (m. p. 48–48.5°). The residue was made acid and was again distilled with steam, but no volatile substance was present, and therefore no naphthol was produced during the reaction.

Identification of the **Products.—a-Naphthylamine** was identified by melting point and mixed melting point with a sample of known purity. Naphthionic acid was identified by conversion to the diazonium salt, according to the method of Erdmann.[9] The diazonium salt thus obtained decomposed instantaneously at 140.5°. It gave characteristic azo dyes with alkaline β-naphthol and with phenol.

A sample of the monosodium salt of the naphthylamine disulfonic acid was crystallized four times from 70% alcohol. It still retained a slight pinkish tint, but was completely free from inorganic salts. It was dried at 140° and analyzed.

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[9] Erdmann, *Ann.*, 24,330 (1888).

Anal. Calcd. for $C_{10}H_8S_2O_6Na$: S, 19.68; Na, 7.07. Found: S, 19.28; Na, 6.94, *7.00*

It is almost certain from these analyses and the method of synthesis that this compound is the monosodium salt of 1-aminonaphthalene-2,4-disulfonic acid, described in an early German patent.[10] No further time was spent on its orientation at this time, as we were interested only in the groups introduced by the reagent and not in their positions.

Experiments with Nitrobenzene

(A) The Standard Procedure.——Fifty grams was reduced in one and one-half hours. The contents of the flask were evaporated to 500 cc., decomposed with 100 cc. of concentrated hydrochloric acid, and re-evaporated to 500 cc. One hundred and twenty grams of solid sodium hydroxide was then immediately added, and the mixture steam distilled. The distillate, on extraction with ether, drying of the ethereal extracts, and distillation, gave 7 g. of aniline, boiling at 181–183" (16%, on the basis of the nitro compound used). The residue from the distillation was filtered, while still hot, from precipitated inorganic salts (sodium chloride and sodium sulfate). On cooling the filtrate to room temperature, crystals were obtained which were rendered almost colorless by repeated washing on the filter with methyl alcohol. These were nearly pure sodium sulfanilate, and when dry, weighed 38 g. (35%).

(B) Bisulfite Followed by Sulfuric Acid.—The standard procedure was followed, using 50 g. of the nitro compound. The reduction stage again required one and one-half hours.[11] One hundred cc. of concentrated sulfuric acid was used to decompose the solution. There were obtained 16 g. (20%) of sulfanilic acid and 12 g. (32%) of pure aniline.

Identification of Sodium Sulfanilate.—Bromination with liquid bromine gave tribromoaniline, identified by melting point and mixed melting point with a reliable specimen. The phosphorus pentachloride reaction product[12] was prepared by heating the sodium salt with phosphorus pentachloride in dry benzene. It melted at 154–155°, whereas the "trichloro compound" of Laar, when very pure, melts at 158'. Oxidation of the sodium salt with chromic acid and sulfuric acid in a current of steam gave benzoquinone, m. p., 113°; mixed m. p. with known sample of quinone, 113'. A purified sample of the sodium salt was analyzed, after drying at 140°.

Anal. Calcd. for $C_6H_6NSO_3Na$: Na, 11.53. Found: Na, 11.77.

Experiments with p-Nitrotoluene

Fifty grams was reduced, according to the standard procedure, in five hours. The mixture was evaporated to 500 cc., and decomposed with 100 cc. of 12 *N* hydrochloric acid. After re-evaporating to 500 cc., the solution was cooled, 100 g. of sodium hydroxide dissolved in 100 cc. of water was added, and this mixture was distilled with steam. From the distillate, 30.5 g. (72%) of nearly pure *p*-toluidine was obtained (m. p., 44.5°; b. p., 198–199°; acetyl derivative, m. p., 147–147.5'). The residue from the steam distillation deposited, on cooling, a white organic salt mixed with sodium chloride and sodium sulfate. This was dissolved in water, filtered hot, and the cooled filtrate acidified with hydrochloric acid. Eight grams (11%) of 4-toluidine-3-sulfonic acid was obtained.

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[10] Meister, Lucius and Brüning, German Patent 92,082, *Friedländer*, 4, 528 (1895).

[11] In one run the standard procedure was varied by diluting with 2000 cc. rather than the usual 500 cc. of water. At this dilution the reduction stage required only forty minutes. A 25% yield of sulfanilic acid was obtained.

[12] Laar, *J. prakt.* Chem., [2] 20, 250 (1879).

Identification of **the** Aminosulfonic Acid.—Bromination gave 3,5-dibromo-4-toluidine, m. p., 70–71°. **A** sample prepared by bromination of *p*-toluidine melted at 74–75°. A mixture of the two melted at 72–73°. The sodium salt (from the aminosulfonic acid and excess dilute sodium hydroxide) lost no weight when heated at 150°. It was analyzed for sodium.

Anal. Calcd. for $C_7H_8SO_3NNa$: Na, 10.99. Found: Na, 10.80, 10.92.

Experiments with o-Nitrotoluene

Using the standard procedure, the reduction required twelve hours. After treatment with 100 cc. of 12 *N* hydrochloric acid, the mixture was allowed to cool. Large, white, silky plates separated, which were filtered. When dry, they weighed 11 g., and proved to be sodium *o*-toluene-sulfaminate. That this salt should precipitate from a solution which was both hot and quite strongly acid was rather unexpected. The filtrate was now boiled on the steam-bath for an hour, cooled again, treated with 100 g. of solid sodium hydroxide, and steam distilled. By extracting the distillate with ether, and evaporating the ether, there was obtained 17 g. (40%) of o-toluidine, boiling at 196–197°; acetyl derivative, m. p., 106–106.4°. The distillation residue was filtered, while hot, from inorganic salts. On cooling, white, lustrous, scaly crystals of sodium 2-toluidine-5-sulfonate were deposited. After drying at 90°, they weighed 27.5 g., or 34% of the calculated yield.

Identification **of** the Sodium **Sulfaminate.**—This salt, when heated at 140–150°, decomposed, losing 23–24% of its weight, and giving a strong toluidine odor. **A** sample, purified until free from sulfate, was boiled with hydrochloric acid, after which it gave a heavy precipitate of barium sulfate when treated with barium chloride, and when made alkaline, it gave a positive carbylamine test, indicating the presence of a primary amine. **A** diazotized sample gave dyes of the same shade as a known solution of diazotized sodium o-tolyl-sulfaminate.

Anal. Calcd. for $C_7H_8NSO_3Na\cdot H_2O$: Na, 10.13. Found: Na, 10.04, 10.15.

Identification of the Sodium Salt of the Amine **Sulfonic** Acid.—Anal. Calcd. for $C_7H_8NSO_3Na$: Na, 11.01. Found: Na, 11.10, 11.13. Oxidation with chromic acid in sulfuric acid gave toluquinone, m. p. 67.5°; m. p. of known sample of toluquinone, 66.5°; mixed m. p., 66.5°. Acidification of a concentrated water solution yielded the free sulfonic acid, which gave reactions characteristic of a substance of its type. Toluquinone was obtained from it, by oxidation as above.

Experiments with 2-Nitro-1,4-xylene

Preparation of **2-Nitro-1,4-xylene.**—*p*-Xylene was nitrated according to Willstatter's chloroform **method.**[13] Ten grams of the hydrocarbon was nitrated at one time. Fractional distillation of the oil resulting from ten nitrations gave 73 g. of 2-nitro-1,4-xylene, boiling at 238–242° (740 mm.).

Reduction of **2-Nitro-1,4-xylene.**—Thirty and seven-tenths g. (0.2 mole) was reduced, using the standard procedure except that 1000 cc. of water was added instead of the usual 300 cc. The products were as follows: 14.8 g. (60%) of 1,4-xylidine (b. p. 218.5°, corr.; acetyl derivative, m. p. 139.7–140°); and 6.2 g. (15.5%) of 2-amino-1,4-xylene-5-sulfonic acid.

Identification of the **Aminosulfonic** Acid.—The diazotized acid gave the usual coupling reactions. 1,4-Xyloquinone was obtained by oxidation with chromium trioxide and dilute sulfuric acid, and identified by the method of mixed melting points. The sodium salt was obtained from the free acid and excess sodium hydroxide as white

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[13] Willstätter, *Ber.*, 42, 4151 (1909).

scale-like crystals, containing two molecules of water of crystallization. Heated at 50–60° it loses one molecule of crystal water, and at 140–150° it loses the second molecule of water. Although Nolting, Witt and Forel[14] and also Nolting and Kohn[15] reported that the salt crystallized water-free, our results indicate that this is not the case.

Anal. (air-dried salt). Calcd. for $C_8H_{10}NSO_3Na\cdot 2H_2O$: Na, 8.87. Found: Na, 8.80, 8.66, 8.77, 8.91, 8.75. (50° dried salt.) Calcd. for $C_8H_{10}NSO_3Na\cdot H_2O$: H_2O, 7.47. Found (by heating at 150° to constant weight): H_2O, 7.51, 7.46. (150° dried salt.) Calcd. for $C_8H_{10}NSO_3Na$: Na, 10.33. Found: Na, 10.46, 10.48.

Experiments with *m*-Dinitrobenzene

(A) Reduction with Neutral **Sulfite.**—The procedure approximated to that used previously by Nietzki.[16] Forty-three grams of m-dinitrobenzene and 400 cc. of a solution (5.2 N) of sodium bisulfite (10% excess on the basis of the reduction of one nitro group) was heated just above the melting point of the solid until, upon cooling, no dinitrobenzene precipitated (two hours). One hundred and twenty-five cc. of 12 *N* hydrochloric acid was then added and the mixture boiled for thirty minutes. Yellow needles of m-nitranilinesulfonic acid separated, which weighed, when dry, 35 g. or 64% of the calculated quantity. They were purified by repeated reprecipitation, with hydrochloric acid, from a sodium hydroxide solution; followed by two recrystallizations from water, and thorough washing on the filter with methyl alcohol. They were dried at 140° and analyzed.

Anal. Calcd. for $C_6H_6O_5N_2S$: S, 14.62. Found: S, 14.16, 14.14.

The filtrate from which the m-nitraniline sulfonic acid separated was made alkaline with sodium hydroxide, the Glauber's salt was filtered off, and the filtrate was extracted with ether. Evaporation of the ether left a small amount of long needles, m. p. 110–112°; m. p. of m-nitraniline, 114°.

(B) Reduction with **Bisulfite.**—Seventy-two grams of the dinitro compound was heated for eight and one-half hours with 500 cc. of 5.2 N sodium bisulfite (110% excess for the reduction of one nitro group), and 500 cc. of water. One hundred cc. of concentrated sulfuric acid was then added. The cooled solution, after evaporation to 500 cc., contained a black cake of solid. This was extracted, first with hot 95% alcohol, and then with hot water. The part insoluble in water was discarded. From the alcohol solution was obtained 5 g. of unchanged dinitrobenzene. From the water solution was obtained about a gram of a substance, which, from its properties and a sulfur analysis on the crude material, was found to be the m-nitraniline-p-sulfonic acid. The filtrate from which this precipitated, on standing in a total volume of 400 cc. for several days, deposited purplish colored crystals, weighing 20 g. They were purified from admixed sodium sulfate by extraction with cold water, leaving 8 g. of an organic substance, which proved to be 1,3-diaminobenzene-4-sulfonic acid. It was identified by its amphoteric nature, the readiness with which it could be diazotized, and its crystalline habits. It crystallized in two distinct modifications—large monoclinic plates and elongated prisms.[17]

Anal. Calcd. for $C_6H_8N_2SO_3$: S, 17.00. Found: S. 16.66, 16.40.

Experiments with *p*-Nitrophenol

The standard procedure was used, except that solid sodium hydroxide was added, equivalent to the phenol used, and in addition to the alkali added normally. From 55.6

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[14] Nolting, Witt and Forel, *Ber.*, 18, 2667 (1885).

[15] Nolting and Kohn, *ibid.*, 19, 141 (1886).

[16] Nietzki, *Ber.*, 29, 2448 (1896).

[17] Cf. Post, *Ann.*, 205, 105 (1880).

g. of p-nitrophenol, 10.5 g., or 14% of the theoretical weight of *p*-aminophenol-*m*-sulfonic acid, was obtained, by extracting the mixture of salts obtained after the acid treatment with water at 30°, and filtering the insoluble portion. It was impossible to isolate any other product, or to increase the yield of the aminosulfonic acid. It is probable, however, that the aminosulfonic acid is the chief product of the reaction, but it is impossible to isolate more of it without resorting to a laborious series of fractional crystallizations of the mixture obtained after the usual acid treatment. (The aminosulfonic acid is soluble in water to the extent of about 3 parts per 100.) Evidence was obtained which indicated the presence of considerable quantities of the aminophenol sulfonic acid in later crystalline fractions and mother liquors. Thus, the pure aminophenolsulfonic acid shows an interesting and characteristic fluorescence—violet in pure water, and bluish-purple in alkaline solution. The acidified solutions do not fluoresce. Now, in an attempt to separate more of the product from the inorganic salts produced in the reaction, after acid treatment, by a process of fractional crystallization, it was noted that all succeeding crystalline fractions, mother liquors, and filtrates showed this same fluorescence. Furthermore, other typical color reactions of this compound persisted throughout these later fractions. Moreover, solutions of p-aminophenol (the other expected product) in aqua ammonia are lavender and do not fluoresce. This affords evidence that very little, if any, of this amine is produced, and that the amount of aminosulfonic acid isolated constitutes but a minimum yield.

Identification of the Aminophenol Sulfonic Acid.—This substance, when heated with 25% sulfuric acid in a sealed tube for six hours at 165–170°, gave p-aminophenol, m. p., 183–183.5° (decomp.); m. p. of a sample of p-aminophenol of known origin, 183.4–183.8° (decomp.); mixed m. p. 182.8–183.2" (dec.). The aminophenol sulfonic acid gave a diazonium sulfate which did not decompose upon boiling with water. This is in accord with the observation of Schultz and Stable,[18] who state that the diazo compound of this aminophenol sulfonic acid is stable toward boiling water. Our diazo salt melted at 171°, after two crystallizations from water. Schultz and Stable report a melting point of 189°. The diazo compound, when heated with 25% sulfuric acid in a sealed tube at 180" for two hours, gave hydroquinone, identified by the method of mixed melting points.

Experiments with p-Nitrobenzoic Acid

Twenty-five grams was reduced according to the standard procedure, except that sodium hydroxide was again added in quantity sufficient to convert the acid to its sodium salt. The reduction stage required four and one-half hours. Fifty cc. of 12 *N* hydrochloric acid was then added and the mixture boiled again for two and one-half hours. Upon cooling, a fluffy, white solid separated, weighing 11 g., when dry. This was shown to be the p-aminobenzoic acid salt of *p*-amino-*m*-sulfobenzoic acid. The filtrate was evaporated to 250 cc. and allowed to stand. A second solid substance separated, weighing, when dry, 6 g.[19] This was shown to be p-aminobenzoic acid sulfate. On further evaporation of the filtrate to 150 cc. and cooling to −10°, a precipitate of 37 g. of Glauber's salt was obtained, and 40 g. more was thrown out by the addition of 250 cc. of 95% alcohol. The Glauber's salt was extracted with hot methyl alcohol. Evaporation of the alcohol left 1.5 g. of p-aminobenzoic acid sulfate. Three grams more was obtained by evaporating the aqueous ethyl alcoholic filtrate to 50 cc., extracting the resulting

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[18] Schultz and Stable, J. prakt. *Chem.*, [2] 69, 336 (1904).

[19] In another run, the filtrate was divided into two parts at this point. One part was extracted with ether as it was, but gave no appreciable ether-soluble material. The other part was made feebly alkaline, and then extracted with ether. Three *grams* of p-aminobenzoic acid was obtained.

precipitate of impure sodium chloride with hot methyl alcohol, and expelling the alcohol. The filtrate was now evaporated to dryness, the residue extracted with hot 95% ethyl alcohol, the alcohol evaporated to a volume of 25 cc. and cooled. A precipitate of 0 5 g. of p-aminobenzoic acid, melting, without purification, at 183–185°, was obtained.

Properties of the **p-Aminobenzoic** Acid Salt of ***p*-Amino-*m*-sulfobenzoic** Acid.—This is an acidic salt, which burns completely without melting. It is soluble in dilute alkali, and is reprecipitated unchanged by dilute acids. It is insoluble in acids, dilute or concentrated, and in ordinary organic solvents. It is practically insoluble in cold water, but appreciably soluble in hot water. Qualitative tests showed that it is neither an amine sulfate nor an amine hydrochloride. It crystallized from water in needles, showing a silky, fibrous nature under the microscope. A sample was purified for analysis by repeated reprecipitation from an alkaline solution (both ammonium and potassium hydroxides were used) with dilute hydrochloric acid, and then by repeated crystallization from water. It was then washed repeatedly on the filter with methyl alcohol and dried at 140°. The analytical results agree most closely with those calculated for a salt consisting of one molecule of p-aminobenzoic acid and one molecule of *p*-amino-*m*-sulfobenzoic acid.

Anal. Subs., 0.2747, 0.2982, 0.3005, 0.2627, 0.3865: $BaSO_4$, 0.1704, 0.1831, 0.1826, 0.1607, 0.2407. Subs., 0.1391, 0.1159: CO_2, 0.2378, 0.1988; H_2O, 0.0543, 0.0422. Calcd. for $C_{14}H_{14}O_7N_2S$: C, 47.5; H, 4.2; S, 9.04. Found: C, 46.7, 46.9; H, 4.0, 4.3; S, 8.53, 8.45, 8.35, 8.37, 8.55. *Titration equivalent.* Subs., 0.4376, 0.4355: 0.2230 N NaOH (phenolphthalein), 16.79, 16.60 cc. Calcd. for $C_{14}H_{14}O_7N_2S$ (tribasic): 16.61, 16.53 cc.

This insoluble salt was split into its components as follows. To 1.1664 g. of an analytically pure sample was added 29.54 cc. of 0.2230 *N* sodium hydroxide, the exact amount calculated to neutralize two mono-acidic groups of a molecule of molecular weight 354. A slight insoluble portion was brought into solution by adding a little water. The solution showed an acid reaction toward litmus. It was extracted thirteen times with ether. The thirteenth extract, evaporated separately, gave 0.003 g. of the ether-soluble material. In all 0.401 g. of this material (p-aminobenzoic acid, m. p. 184–185°) was obtained.

Titration equivalent. 0.2301 g. required 7.63 cc. of 0.2230 *N* NaOH. Calcd. for $C_7H_7O_2N$ (monobasic), 7.54 cc.

To the water solution was added hydrochloric acid until a precipitate formed This weighed 0.1152 g., after drying at 80° and required 4.36 cc. of 0.2230 N NaOH. Calcd. for $C_{14}H_{14}O_7N_2S$: 4.37 cc. Thus it appears that thirteen extractions with ether did not remove quite all of the p-aminobenzoic acid. When acid was added, this precipitated as the *least soluble salt* of the ions present in the solution, namely, as the aminosulfobenzoic acid salt. Since 0.115 g. of this salt is equivalent to 0.044 g. of *p*-aminobenzoic acid, the total yield of the latter was $0.401 + 0.044 = 0.445$ g.; calculated for 1.1664 g. of the salt, 0.451 g.[20] The filtrate, after separation of the salt, was evaporated to a small volume. This gave 0.51 g. of a white substance (dried at 115°). This was a sulfur-containing acid which crystallized from water in small plates characteristic of p-amino-m-sulfobenzoic acid.[21]

Titration equivalent. 0.2659 g. required 10.90 cc. of 0.2230 N NaOH. Calcd. for $C_7H_7O_5NS$ (dibasic): 11.00 cc.

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[20] In a previous run, in which only three extractions with ether were made, 0.27 g. of aminobenzoic acid as such, and 0.155 g. as the reprecipitated salt, or a total of 0.425 g., was obtained from 1.116 g. of the substance; calculated, 0.432 g.

[21] Cf. Van Dorssen, *Rec. trav. chim.*, *29*, 373 (1910); Scott and Cohen, *J. Chem. Soc.*, 123, 3180 (1923).

Identification of *p*-Aminobenzoic Acid Sulfate.—A sample was dissolved in the least possible *N* potassium hydroxide, and carefully acidified with 2 N hydrochloric acid. At the neutral point, a substance precipitated which was identified as *p*-aminobenzoic acid by mixed melting points. With bromine water it gave trihromoaniline and an ammonia soluble substance. The latter, after reprecipitation with acid, showed a decomposition range of 266–286°. (Reported by Sudborough for dibromo-*p*-aminobenzoic acid, 260–270°.)

Summary

1. A number of aromatic nitro compounds have been reduced with sodium bisulfite, and the solutions thus obtained have been boiled with mineral acids.

3. The quantities of amines and aminosulfonic acids which are produced in this manner have been determined.

3. Several other reduction products have been isolated and identified.

4. A standard procedure for studying the Piria reaction has been adopted, and comparable results thereby obtained.

5. Factors have been pointed out which affect the reaction and require further investigation.

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

THE PIRIA REACTION. II. THE ROLE OF THE SULFAMINIC ACIDS[1,2]

BY W. H. HUNTER AND MURRAY M. SPRUNG

RECEIVED NOVEMBER 28, 1930 PUBLISHED APRIL 6, 1931

When the acid treatment which follows the reduction of a nitro compound in the "over-all" Piria reaction[3] is omitted, the principal product which can be isolated is a sulfaminic acid salt, of the general formula $RNHSO_3M$. The isolation of an N-sulfonated compound of this type was included among the original findings of Piria,[4] and thereafter similar products were mentioned by other early investigators.[5] However, that these sulfaminic salts were the *chief* products of the reaction when acid treatment was avoided was first emphasized by Weil,[6] who investigated a variety of aromatic nitro compounds, including alkyl nitrobenzenes,

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[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September 1928.

[2] Presented before the Division of Organic Chemistry of the American Chemical Society at the Minneapolis Meeting, September 9–16, 1929.

[3] Hunter and Sprung, THIS JOURNAL, 53, 1432 (1931).

[4] Piria, *Ann.*, **78,** 31 (1851).

[5] Hilkenkamp, *ibid.*, 95, 86 (1885); Smit, *Ber.*, 8, 1442 (1875).

[6] (a) Weil, German Patents 147,552 and 151,134, *Friedländer*, 7, 58, (b) 61 (1902); (c) Weil and Moser, *Ber.*, 55, 732 (1922); *(d)* Weil and Wassermann, *ibid.*, 55, 2533 (1922).

the alkyl esters of nitrocarboxyiic acids, acylaminonitro compounds, nitrophenols, nitroamines and halogenated nitro compounds.

This consideration alone suggests a reasonable mechanism for the course of the "over-all" Piria reaction, which may be stated as follows: in the reduction stage, the nitro group is reduced to an amine or a sulfaminic acid or both; in the acid treatment stage, the sulfaminic acid is partly hydrolyzed to sulfuric acid and the same amine, and is partly rearranged to an aminosulfonic acid. In fact, it was this simple conception of the reaction which we set up as a working hypothesis at the start of our work. It is readily suggested by two considerations.

1. Many investigators have shown that the salts of sulfaminic acids are converted into aminosulfonic acids by baking, and in one or two cases the same is true of the free acid.[7]

2. Weil especially[6b] has pointed out that the addition of concentrated mineral acid aids the transformation of sulfaminic acids to the aminosulfonic acid derivatives. In more or less vague terms, other investigators have mentioned the same reaction.[8]

Against the hypothesis must be considered four opposed considerations.

1. The statement of certain investigators that "dilute" mineral acids hydrolyze the sulfaminic acids quantitatively,[9] though we were unable to find any who stated the concentration of acid used, or gave any quantitative data in support of this contention.

2. Weil himself, in another place,[6b] explicitly states that he does not believe that the sulfaminic acids are transformed into the aminosulfonic acids. He suggests that sulfonation may actually occur in the reduction stage, but offers no experimental evidence, nor any theoretical reason for his opinion.

3. Raschig[10] has suggested a mechanism of formation of sulfaminic acids and amino sulfonic acids, from a hypothetical common intermediate, an arylimino disulfonate, $ArN(SO_3Na)_2$.[11]

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[7] Junghahn, *Ber.*, **35, 3747 (1890);** Seyewitz and Block, ***Bull. soc. chem.***, *[4]* **1, 320 (1907);** Seyewitz and Noel, ***ibid.***, **[4]** *3*, **497 (1908);** Quilico, ***Gazz. chim. ital.***, ***56*, 620 (1926);** De Ruijter de Wildt, ***Rec. trav. chim.***, **23, 173 (1904);** Bamberger and Hindermann, ***Ber.***, 30,654 **(1897).**

[8] We know of only one set of experiments concerning the effect of concentrated acids on sulfaminic acids which was both carefully performed and adequately reported, that of Bamberger and Kunze [*Ber.*, 30, 2274 (1897)], who showed that potassium phenylsulfaminate, when treated with a few drops of concentrated sulfuric acid in glacial acetic acid and allowed to stand for eighty hours in the ice box, was converted to *o*-anilinesulfonic acid and that this, in turn, could be converted to sulfanilic acid by heating at 180–190° with concentrated sulfuric acid.

[9] See, for example, Traube, ***Ber.***, **23, 1653 (1890);** ***ibid.***, **24,360 (1891);** Junghahn, ***ibid.***, **31, 1234 (1898).**

[10] Raschig, "Stickstoff and Schwefel Studien," Verlag Chemie G. m. b. H., Berlin, **1924,** pp. 255–272.

[11] The isolation of a compound of this type has recently been reported by Engel

$$NaSO_3—Ar—NHSO_3Na \xleftarrow{\text{Rearr.}} ArN(SO_3Na)_2 \xrightarrow{\text{Hydrolysis}} ArNHSO_3Na$$

4. Disulfonic acids have been isolated at the end of the acid treatment stage,[12] and their presence is unaccounted for by any scheme ever suggested.

Viewing these conflicting ideas, it seemed that the first constructive step would be to ascertain, not whether sulfaminic acids could be rearranged, but whether they could be rearranged by acid of the concentrations ordinarily used in the acid treatment stage of the Piria reaction. Our own practice being to bring the reaction mixture to a concentration in the neighborhood of 2 *N* with respect to hydrochloric acid, it was decided to take representative sulfaminic acids and subject them to the action of a wide range of acid concentrations on each side of this point, in order to attain quantitative certainty on this single point. At the same time, it was planned that if two parallel reactions were actually found, kinetic studies would be carried out. The event showed, however, that over the range of concentration from about 0.5 to 5.35 N, only hydrolysis occurs. Though the opinion that the sulfaminic acids were not the precursors of the aminosulfonic acids has already been expressed, we believe that this is the first time that quantitative data of this type have been brought forward to settle the point.

Experimental Method

A definitely standardized procedure was employed. Several of the sodium salts of sulfaminic acids were prepared and purified. Weighed samples of these salts (contained in 50-cc. Erlenmeyer flasks) and measured volumes of a standardized hydrochloric acid were brought to temperature in a thermostat. Then the acid was added to the sulfaminate, the flask stoppered, and replaced in the thermostat until the reaction was complete.[13] The contents of the flask were then washed out into a beaker, heated to boiling and a boiling solution of barium chloride added. The precipitate of barium sulfate was filtered, washed, dried and weighed. The weight of sulfuric acid produced was calculated from the weight of the barium sulfate.

Materials

The sodium sulfaminates were prepared by the action of partially neutralized sodium bisulfite upon the corresponding nitro compounds, and

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[THIS JOURNAL, 51, 3483 (1929)] in a paper dealing with the cleavage of azo compounds by alkali sulfites.

[12] For example, Walter, German Patent 109,487, *Friedländer*, 5, 70 (1899); Bucherer and Borsch, *J. prakt. Chem.*, [2] 111, 329 (1925); Meister, Lucius und Brüning, German Patent 92,082, *Friedländer*, 4, 528 (1895); and numerous other patent citations.

[13] Preliminary runs, made to determine approximate speeds, indicated that with the most dilute acid used (ca. 0.5 N) the reactions were complete in about forty hours at 40°. The later runs were made in the neighborhood of 50°.

purified by repeated crystallization from water to which a few drops of alkali were added to prevent decomposition. In some cases it was impossible to free them entirely from admixed inorganic salts.

Sodium Phenyl **Sulfaminate.—This** is the most soluble of the salts used, and consequently was the most difficult to purify. After five recrystallizations from water, appreciable quantities of sodium chloride and sodium sulfate were still present. Therefore, to characterize the sulfaminate a small amount of the compound, further recrystallized until free from these salts, was dried for several days in a vacuum desiccator over calcium chloride. On analysis, it was found to contain one molecule of water of crystallization.

Anal. Calcd. for $C_6H_6NSO_3Na \cdot H_2O$: Na, **10.81.** Found: Na, **10.85, 10.90.**

The material which had been crystallized five times was then analyzed and found to contain **6.55%** of sodium chloride, **4.78%** of sodium sulfate and **13.99%** of sodium, total. The composition of the sample was therefore as follows

Na_2SO_4, %............	**4.78, equiv.** to	2.62% Na
NaCl, %..............	6.65, **equiv.** to	1.55% Na
$C_6H_6NSO_3Na \cdot H_2O$, %...	88.58, **equiv.** to	**9.574** Na
	Total	13.74% Na
	Found **by** analysis,	**13.99%** Na

Sodium p-Tolyl **Sulfaminate.—The** salt was purified by several recrystallizations from water and dried in a vacuum desiccator for seven days.

Anal. Calcd. for $C_7H_8NSO_3Na$ (anhydrous): Na, **11.01.** Found: Na, **11.19, 11.28.**

There was still a slight admixture of sodium sulfate, which caused the sodium analysis to be higher than the theoretical. A **0.4-g.** sample gave **0.0071** g. of barium sulfate, equivalent to 0.0030 g. of sulfuric acid, or **1.08%** of sodium sulfate.

Sodium o-Tolyl **Sulfaminate.—A** sample was crystallized from water until free from sodium sulfate. It was dried in a vacuum desiccator over calcium chloride for four days.

Anal. Calcd. for $C_7H_8NSO_3Na$ (anhydrous): Na, **10.13.** Found: Na, **10.25.**

Sodium p-Acetaminophenyl **Sulfaminate.—The** salt was crystallized **from** water until free from inorganic impurities and dried *in vacuo* over calcium chloride for sixty hours. It contained two molecules of water of crystallization.

Anal. Calcd. for $C_8H_9O_4N_2S \cdot 2H_2O$: Na, **8.00.** Found: Na, **8.18, 8.15.**

Results

The sodium sulfaminates were allowed to react with solutions of hydrochloric acid varying in concentration from 0.47 to **5.35** N. The results thus obtained are presented in tabular form.

ANALYTICAL DATA ON THE REACTION BETWEEN SODIUM **SULFAMINATES** AND HCl[a]

Salt used	Runs	Sample, g.	**Acid normality, max. and min.**	**H_2SO_4, calcd. for 100% hyd., g.**
$C_6H_5NHSO_3Na \cdot H_2O$[b]	4	0.4	0.47–5.35	0.1755
p-$CH_3C_6H_4NHSO_3Na$[c]	3	.4	0.47–2.70	.1887
o-$CH_3C_6H_4NHSO_3Na$	3	.3	1.05–5.35	.1295
p $CH_3CONHC_6H_4NHSO_3Na \cdot 2H_2O$	4	.4	1.07–5.35	.1362

H_2SO_4 found, g. (av.)	Av. dev. from mean, g.
0.1765	0.0021
.1894	.0022
.1287	.0029
.1346	.0004

[a] The reactions were carried out at temperatures between 47–50°, varying not more than ±1° during a given run. [b] The sample contained 4.78% of sodium sulfate, as mentioned above. The sulfate due to this admixture was, of course, considered in the calculations. [c] The sample contained 1.08% sodium sulfate. The correction was applied as before.

For all four of these salts the quantity of sulfuric acid produced was therefore, within analytical error, the amount which should have resulted from complete hydrolysis of the sulfaminate to the corresponding amine and sulfuric acid. This was true for all acid concentrations.

According to the standard procedure used in the study of the "over-all" Piria reaction,[3] the solutions were approximately 2 normal with respect to hydrochloric acid, after the addition of this reagent. Since the quantitative experiments covered a sufficiently wide range of concentrations on either side of this figure, we consider this to be definite proof that sulfaminic acids play no part in the production of nuclear sulfonated compounds during the Piria reaction.

The investigations are being continued in the attempt to discover the intermediate which does give rise to the sulfonated amines.

Conclusions

Several sodium salts of sulfaminic acids have been prepared and carefully purified, and their reactions with varying concentrations of hydrochloric acid studied. It has been shown that with acid concentrations from 0.5 to 5.35 normal, these sulfaminates hydrolyze quantitatively to sulfuric acid and the corresponding amines, giving absolutely no trace of aminosulfonic acids.

Hence the aminosulfonic acids which are produced by the "over-all" Piria reaction are certainly not formed by rearrangement of sulfaminic acids.

It is worthy of passing notice that this work affords one more instance of a suspected indirect substitution, which in fact does not occur.

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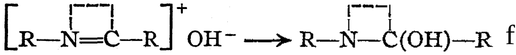
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY AND OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE

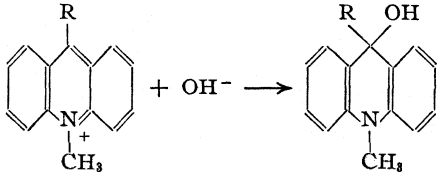
PSEUDO BASES. II. EQUILIBRIA AND RATE OF CHANGE OF TAUTOMERIC BASES IN THE PYRAZINE SERIES. THE EFFECT OF CONJUGATION

BY JOHN G. ASTON

RECEIVED DECEMBER 5, 1930 PUBLISHED APRIL 6, 1931

In this paper is described a kinetic study of the reaction of sodium hydroxide on certain quaternary pyrazinium salts, namely, 1,2,5-trimethylpyrazinium iodide, 1,2,2,5,5-pentamethyldihydropyrazinium iodide and 1,2,2,3,5,5,6-heptamethyldihydropyrazinium iodide, using a conductivity method to follow the progress of the reaction. The bases isolated from these salts were described in the first paper of this series.[1] Further information upon the relationship of these bases to the other possible tautomeric forms is now presented.

Hantzsch and Kalb,[2] in their work on pseudo bases, made a kinetic study of the reaction between aqueous potassium hydroxide and N-methylpyridinium, N-methylquinolinium and N-methylacridinium salts, using a conductivity method to measure the concentration of strong base, and showed that in the first two cases the equilibrium in the system  $[\mathrm{R{-}N{=}C{-}R}]^{+}\ \mathrm{OH}^{-} \longrightarrow \mathrm{R{-}N{-}C(OH){-}R}$ favored the strong quaternary base. In the case of 5-phenyl-10-methylacridinium sulfate quite anomalous results were obtained which were not at all in keeping with the reaction which they postulated



as the rate determining step. However, the compound isolated from the reaction has all the properties of the pseudo base.

Preliminary experiments consisting of solubility determinations described in this paper have shown that the rate determining step is probably the crystallization of the so-called "pseudo base" from the solution and that in the reaction written above the equilibrium is shifted to the right in virtue of the insolubility of the product.

No similar anomalies were found in the pyrazine series, where all the bases are soluble in water. Here there is certain evidence for the type of

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[1] Aston, THIS JOURNAL, 52, 5254 (1930).

[2] Hantzsch and Kalb, *Ber.*, 32, 3109 (1899).

reaction postulated by Hantzsch in addition to reactions of an entirely different type. These were discussed in the previous paper.

Experimental Method and Results

Preparation of Materials.—1,2,5-Trimethylpyrazinium iodide was recrystallized from absolute alcohol to constant analysis. 1,2,2,5,5-Pentamethyl and 1,2,2,3,5,5,6-heptamethyldihydropyrazinium iodide were recrystallized from methyl alcohol–*n*-butyl alcohol mixtures to constant analysis.

Conductivity water was prepared by distillation from alkaline permanganate with the usual precautions. Its specific conductance was always less than 2 × 10^{-6} ohm^{-1} cm.$^{-1}$.

Sodium hydroxide solutions of known concentration were prepared by dilution of an accurately standardized carbonate-free stock solution with conductivity water.

Standard hydrochloric acid solutions were prepared by dilution of constant boiling hydrochloric acid with conductivity water and their strengths checked gravimetrically. Potassium chloride, used for cell constant determination, was recrystallized to constant conductivity.

Apparatus for Measuring Conductivities.—A Wheatstone bridge arrangement was used.[3]

A calibrated Kohlrausch slide wire bridge with end coils, an enclosed dial six decade resistance box, wound for use with high frequencies, and Brown tunable telephone receivers with a total resistance of 120 ohms were used. The alternating current (1000 cycles) was furnished by a microphone hummer. These instruments were those furnished by Leeds and Northrup. The bridge was neither grounded nor shielded.[4] The lead resistances were each 0.05 ohm. The capacity of the conductivity cell was balanced in all measurements with suitable fixed and variable radio condensers. Readings were always taken within a few tenths of a per cent. of the center of the bridge. A thermostat was used which kept constant temperature to 0.01°. It was filled with ordinary water grounded through the cooling coils. Temperatures were measured accurately to 0.05° by thermometers certified by the Bureau of Standards.

Weights and volumetric apparatus were calibrated.

Conductivity of 1,2,5-Trimethylpyrazinium Iodide.—Washburn conductivity cells were used, Type B for solutions above 0.002 N and Type A for more dilute solutions. The constant of cell B was determined at 25.11° to 0.03% using a solution containing 0.7455 g. of potassium chloride in 500 cc., which has a specific conductance of 0.002770 at 25.10° according to Kohlrausch.[5] The Kohlrausch standard was used because the data were to be used in conjunction with other data using this standard. The constant of cell A was measured to 0.05% by intercomparison with cell B.

The 1,2,5-trimethylpyrazinium iodide used was found to have an equivalent weight of 252.8 (calcd., 250.05) by the Volhard method. Solutions were made up by dissolving weighed quantities of salt and diluting to a known volume with conductivity water. The found equivalent weight was used in computing the normality. All conductivity measurements were made at 25.11° with a precision of at least 0.05%. The results are given in Table I.

The values of the specific conductance (Col. 2) have been corrected for the specific conductance of the water. The limiting equivalent conductance Λ_0 was obtained using the extrapolation method of Randall.[6]

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[3] Washburn and Bell, This Journal, 35, 177 (1913).

[4] See Jones and Josephs, ibid., 50, 1049 (1928).

[5] Landolt–Börnstein–Roth–Scheel, "Tabellen," 1923, p. 1098.

[6] Randall, This Journal, 38, 788 (1916).

TABLE I

CONDUCTIVITY OF 1,2,5-TRIMETHYLPYRAZINIUM IODIDE AT 25°

G. per liter	Specific conductance ohm^{-1} cm.$^{-1}$ × 10^3	Concn. eqts. per liter × 10^2	Λ	$\frac{\Lambda}{\alpha \text{ LiIO}_3}$
15.758	5.467	6.235	87.65	106.9
7.878	2.953	3.115	94.75	109.95
3.950	1.5705	1.5630	100.5	112.3
1.971	0.8143	0.7795	104.5	113.4
0.9830	.4153	.3889	106.8	113.4
.24575	.1081	.09720	113.1	114.8
	Extrapolated 0		115.0	

The values of the equivalent conductance Λ (Col. 4) were divided by $\alpha = \Lambda/\Lambda_0$ for lithium iodate at 18° at the same concentration, obtained from his tables. The quotients thus obtained (Table I, Col. 5) were plotted against $\sqrt{C}$ and the curve extrapolated to zero concentration. The value of Λ_0 thus obtained was checked by reference to the Λ/Λ_0 values for hydrochloric acid. The two agreed within 0.4%. By subtracting the value of the limiting conductance of the iodide ion at 25.11° ($\Lambda_{0I} = 76.7$)[7] from this value of Λ_0, the limiting conductance of the positive ion is found to be $\Lambda_{0Py^+} = 38.3$ at 25.11°.

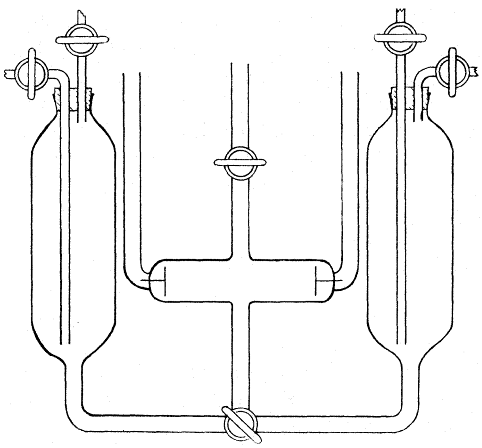
Fig. 1.—Mixing apparatus and cell.

By the use of indicators it was estimated that the basic nitrogen atom in 1,2,5-trimethylpyrazinium iodide had a basic dissociation constant of less than 3×10^{-10}, corresponding to less than 0.02% dissociation in 0.001 N solution. The effect of basic dissociation is thus not detectable in our measurements and does not affect the value of the limiting conductance.

Kinetics of the Reaction of 1,2,5-Trimethylpyrazinium Iodide and Sodium Hydroxide.—The mixing apparatus and cell used in this reaction is illustrated in Fig. 1.

The quantities of the solutions of alkali and salt to be mixed were placed, respectively, in the two cylinders, which were then swept out with a current of carbon dioxide-free nitrogen and allowed to reach the temperature of the thermostat. The solutions were then mixed by forcing the contents of one cylinder completely into the other. The start of the reaction was taken as the end of this operation. Thorough mixing was effected by a

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[7] Noyes, THIS JOURNAL, 34, 479 (1912).

current of nitrogen and forcing the mixture back and forth from one cylinder into the other. The solution was then forced into the conductivity cell, which had been previously swept with nitrogen. The constant of this cell was determined as previously. A measurement of the conductivity of the mixture was made as soon as possible after mixing and at

TABLE II

CHANGE OF SPECIFIC CONDUCTANCE AND CALCULATED CONCENTRATIONS AFTER MIXING 25 CC. OF 0.06236 *N* SODIUM HYDROXIDE AND 25 CC. OF 0.06236 *N* 1,2,5-TRIMETHYLPYRAZINIUM IODIDE AT 25.11"

Time, min.	Specific conductance ohm^{-1} cm.$^{-1}$ × 10^3	$(Py^+) = (OH^-)$ moles/liter × 10^2	k_3, min.$^{-1}$	k_4, min.$^{-1}$ × 10^{-3}
0	8.913	3.118	..	..
8.42	7.390	1.897	..	..
11.92	7.025	1.708	85.75	5.02
22.22	6.419	1.405	71.8	5.11
42.5	5.840	1.120	68.2	6.09
73.8	5.435	0.916	60.8	6.64
112.9	5.145	.776	59.2	7.63
142.6	5.007	.704	59.3	8.42
180.2	4.878	.638	58.3	9.14
210.4	4.799	.597	54.4	9.12
264.3	4.689	.545	51.9	9.53
339.7	4.581	.492	49.0	10.0
408.9	4.509	.456	48.4	10.6
506.9	4.435	.419	..	..

TABLE III

CHANGE OF SPECIFIC CONDUCTANCE AND CALCULATED CONCENTRATIONS AFTER MIXING 25 CC. OF 0.01542 *N* SODIUM HYDROXIDE AND 25 CC. OF 0.01542 *N* 1,2,5-TRIMETHYLPYRAZINIUM IODIDE AT 25.11°

Time, min	Specific conductance ohm^{-1} cm.$^{-1}$ × 103	$(Py^+) = (OH^-)$ moles/liter × 10^2	k_3, min.$^{-1}$	k_4, min.$^{-1}$ × 10^{-3}	k_3 calcd., min.$^{-1}$
0	2.563	0.771	..	..	..
7.3	2.519	.750	..	..	..
19.5	2.445	.715	69.9	9.77	Ref.
32.3	2.389	.687	..	..	..
45.3	2.329	.658	68.5	10.0	68.4
69.5	2.240	.615	..	..	67.2
88.5	2.185	.590	66.4	11.2	66.3
114.7	2.117	.557	..	..	65.5
143.3	2.056	.528	65.5	12.4	64.6
190.2	1.972	.488	63.5	13.0	63.4
322.2	1.814	.413	62.3	15.1	61.0
411.8	1.741	.379	60.3	15.9	60.0
1133.5	1.4761	.2547	55.8	21.9	55.9
1323.6	1.4425	.2391	54.8	22.9	55.3
1638.4	1.4000	.2193	51 4	23.4	54.6
2173.5	1.3518	.1966	44.1	22.4	53.9
2871.5	1.3147	.1793	..	..	..

TABLE IV

CHANGE OF SPECIFIC CONDUCTANCE AND CALCULATED CONCENTRATION AFTER MIXING 25 CC. OF 0.03128 *N* SODIUM HYDROXIDE AND 25 CC. OF 0.01564 *N* 1,2,5-TRIMETHYLPYRAZINIUM IODIDE AT 25.11°

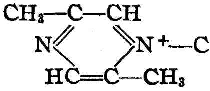
Time, min.	Specific conductance ohm^{-1} cm.$^{-1}$ × 10^3	(Py$^+$) moles/liter × 10^2	(OH$^-$) moles/liter × 10^2	k_3, min.$^{-1}$	k_4, min.$^{-1}$ × 10-	k_3 calcd., min.$^{-1}$
0	4.367	0.782	1.564	..	..	..
9.5	4.229	.716	1.499	83.9	5.60	89.2
12.5	4.189	.696	1.477	85.1	5.76	88.7
18.0	4.126	.665	1.446	82.4	5.69	88.1
32.2	3.992	.600	1.382	77.7	5.62	86.7
47.7	3.881	.545	1.327	85.2	6.42	85.3
84.3	3.696	.456	1.238	78.2	6.32	83.3
119.5	3.572	.3953	1.177	78.1	6.64	81.9
162.5	3.465	.3435	1.126	77.1	6.84	80.6
248.7	3.323	.2746	1.057	79.7	7.54	78.9
334.6	3.230	.2302	1.012	80.2	7.92	77.8
445.8	3.149	.1913	0.973	80.4	8.26	76.8
556.5	3.091	.1638	.946	80.6	8.52	76.1

convenient intervals thereafter. Times were measured using an ordinary watch except for the first part of the reaction, when a stop watch was used. The conductivity of the mixture at zero time was obtained by extrapolation. Representative results of runs at different concentrations are given in the Tables II, III, IV.

In Cols. 1 and 2 are given, respectively, the time after the start of the reaction (*t*) and the value of the specific conductance (κ) of the reacting solution at that time. Duplicate experiments showed that values of κ were reproducible to 0.1%.

Initially the reacting solution contains the ions

Na^+, I^-,



(denoted by Py$^+$) and OH−

Its initial conductivity shows that the base formed from the last two ions is a strong electrolyte. The fall in conductivity is due to the change of this base into one very much weaker whose dissociation will be assumed to be negligible. The four strong electrolytes which can be formed from the above ions will be assumed to be completely dissociated. In Tables II and III, Col. 3, and Table IV, Cols. 3 and 4, the calculated concentrations of Py$^+$ and OH− are given.

At the end of the runs where equivalent quantities of the salt and sodium hydroxide are mixed, the final solution will contain the weak base and sodium iodide at concentrations equal to those of the reactants, $a = b$, at the start. At any previous time during the reaction, the composition of the solution with respect to the ions would be reproduced by adding 1,2,5-trimethylpyrazinium hydroxide (x equivalents per liter) to the final solution until the conductivity reached the measured value, assuming the effect of the weak base to be negligible, so that $(\mathrm{Py}^+) = (\mathrm{OH}^-) = x$.

In the run with the sodium hydroxide in excess of the pyrazinium salt, their initial stoichiometrical concentrations in the mixture being, respectively, a and b, the final concentrations of sodium iodide and sodium hydroxide are b and $(a - b)$ at any previous time $(\mathrm{Py}^+) = x$ and $(\mathrm{OH}^-) = x + a - b$, where x has the same significance as before.

If Λ/Λ_0 were unity for all the electrolytes, x could be calculated from the difference between the observed and final values of the specific conductance using the value of Λ_0 for the pyrazinium hydroxide. As this was not the case, x was calculated by a method similar to that which Sherrill used to calculate the conductivity of mixtures of potassium sulfate and sodium chloride.[8] This method gave values accurate to 0.1%. Although based on the theory of constant ion mobility and incomplete dissociation, its validity as an empirical method is not altered when complete ionization is assumed. It amounts to applying corrections for the changing deviation of the Λ/Λ_0 values from unity. In making the calculations the following data were used: limiting conductances of the four ions at 25.11°, $\Lambda_{0\mathrm{Na}^+} = 51.3$, $\Lambda_{0\mathrm{I}^-} = 76.7$, $\Lambda_{0\mathrm{OH}^-} = 193.0$,[9] $\Lambda_{0\mathrm{Py}^+} = 38.3$, and also plots of "$K$" $= (\Lambda/\Lambda_0)^2C/1 - \Lambda/\Lambda_0$ against $\Sigma i = \Lambda/\Lambda_0 C$ for sodium iodide, sodium hydroxide, 1,2,5-trimethylpyrazinium iodide and its hydroxide for which the following values were used: NaI:Σi: 0.05439, 0.02800, 0.00733; "K": 0.3639, 0.2428, 0.1119;[10] NaOH:Σi: 0.04421, 0.01818, 0.00943, 0.00829, 0.006698; "K": 0.6635, 0.3743, 0.2809, 0.2469, 0.2324;" PyI: Σi: 0.04752, 0.02568, 0.01366, 0.007085; "K": 0.1522, 0.1202, 0.09433, 0.07085. Values of Σi and "K" for the pyrazinium hydroxide were obtained from the extrapolated zero time value of the specific conductance in each of the runs where the concentrations of all the substances present are known, using the Σi — "K" curves for the other three salts and the limiting conductances of the four ions, by a method obvious from the definitions of these quantities and the calculations in Sherrill's paper.

The values thus obtained were: PyOH:Σi: 0.05028, 0.02153, 0.01413; "K": 0.7585, 0.2012, 0.1647. Comparison with the values of "K"

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[8] Sherrill, THIS JOURNAL, 32, 741 (1910).

[9] Values obtained from the tables of Noyes and Falk, THIS JOURNAL, 34, 479 (1912), the temperature coefficients of Kohlrausch, Landolt–Börnstein–Roth–Scheel, "Tabellen," 1923, p. 1104, and the data of Randall and Scalione for NaOH, THIS JOURNAL, 49, 1491 (1927).

[10] From the data of Jones, Landolt–Börnstein–Roth–Scheel, "Tabellen," 1923, p. 1091.

[11] From the data of Randall and Scalione, Ref. 9.

for sodium hydroxide shows that the base is a strong electrolyte. The calculation of x from the observed specific conductances is most simply made by Plotting for each run the concentration of pyrazinium hydroxide against the specific conductance, calculated by Sherrill's method for mixtures of sodium iodide and sodium hydroxide at the fixed concentrations b and $a - b$, with the pyrazinium hydroxide at various rounded concentrations. Values of x are then read from the plot.

The values of k_3 in Tables II and III, Col. 4, and Table IV, Col. 5, are calculated from the equation

$$\frac{d(Py^+)}{dt} = \frac{d(OH^-)}{dt} = k_3(Py^+)^2(OH^-) \tag{1}$$

applying to the consecutive reactions

$$2Py^+ + OH^- \longrightarrow (products)^+ \tag{a-1}$$

$$(products)^+ + OH^- \longrightarrow products \tag{a-2}$$

(a-1) controlling the rate $d(Py^+)/dt$.

Those of k_4 in Tables II and III, Col. 5, and Table IV, Col. 6, are calculated from the equation

$$\frac{d(Py^+)}{dt} = \frac{d(OH^-)}{dt} = k_4(Py^+)^2(OH^-)^2 \tag{2}$$

applying to the reaction

$$2Py^+ + 2OH^- \longrightarrow products \tag{b}$$

Both k_3 and k_4 are instantaneous values calculated by the method of Bray,[12] using the slopes of tangents to plots of $1/(2Py^+)^2$ against the time when $(Py^+) = (OH^-)$ and of $1/(Py^+)$ against the time when $(OH^-) > (Py^+)$. The plot of $1/2(Py^+)^2$ against time for the data in Table III is shown in Fig. 2. The values of k_3 and k_4 are accurate to about 5%. **A comparison** between trends of their values points to a simultaneous disappearance of base by reactions (a-1) and (b), whence

$$\frac{d(Py^+)}{dt} = k'_{iii}(Py^+)^2(OH^-) + k'_{iv}(Py^+)^2(OH^-)^2 \tag{3}$$

where k'_{iii} and k'_{iv} are, respectively, the true specific reaction rate constants of (a-1) and (b). Combination of (1) and (3) gives

$$k_3 = k'_{iii} + k'_{iv}(OH^-) \tag{4}$$

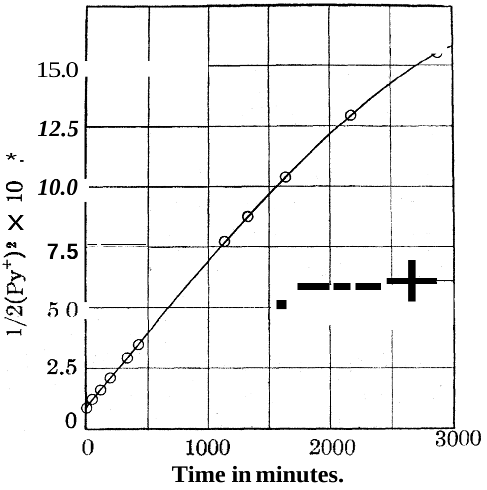

Fig. 2.—*Graph from data* in Table III.

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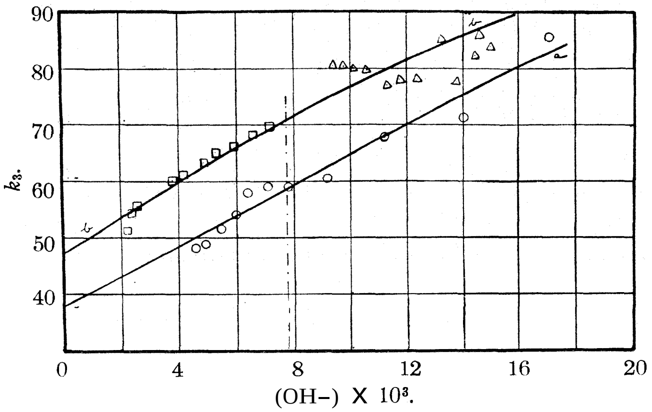
[12] Bray, *J. Phys. Chem.*, 9, 573 (1906).

Since k'_{iii} and k'_{iv} will vary with the salt concentrations, for any particular starting concentrations (4) defines a curve. If such a curve can be extrapolated to (OH−) = 0 at this point $k_3 = k'_{\text{iii}}$ gives the value of k'_{iii} at the total salt concentration which the solution reaches when (OH−) = 0. Thus, in general, (4) defines a family of curves. In Fig. 3 the values of k_3 for each of the runs are plotted against (OH−). The data of Tables II and III lie on two distinct curves aa and bb. Extrapolation of each curve to (OH−) = 0 gives $k'_{\text{iii}} = 38$ and $k'_{\text{iii}} = 47$, respectively. The only electrolyte present at (OH−) = 0 in both cases is sodium iodide at concentrations 0.03118 and 0.00771, respectively. According to the Brönsted[13] theory of reaction rate, the limiting relation for the effect of salts on the specific reaction rate constant k' for a reaction between ions of the type, $2A + B \longrightarrow$ products, is



⊙, Table II; ⊡, Table III; △, Table IV.

Fig. 3.—Effect of (OH−) and concn. of total salt on k_3.

$$\log k' = \log k + (Z_A^2 + 2Z_AZ_B)\sqrt{\mu}$$

where μ is the ionic strength of the solution and Z_A and Z_B are the charges on the ions, k being the value of the constant when $\mu = 0$.

For the above reactions where all the electrolytes are uni-univalent, μ is the total concentration of electrolyte, $Z_A = +1$ and $Z_B = -1$ whence

$$\log k'_{\text{iii}} = \log k_{\text{iii}} - \sqrt{\mu} \tag{5}$$

Similar considerations give rise to the limiting equation

$$\log k'_{\text{iv}} = \log k_{\text{iv}} - 2\sqrt{\mu} \tag{6}$$

for calculating the effect of salt on k'_{iv}. Using (5) and the value of $k'_{\text{iii}} = 47$ at $\mu = 0.00771$ obtained by extrapolation of bb to (OH−) = 0, it is found that $k_{\text{iii}} = 57.5$ at $\mu = 0$ and that $k'_{\text{iii}} = \mathbf{38.3}$ at $\mu = 0.03118$. The agreement of this value with that obtained by extrapolating curve aa

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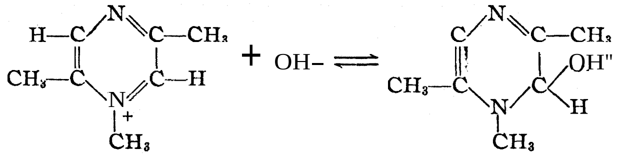
[13] Bronsted, Z. *physik.* Chem., 102, 169 (1922); Bronsted and Livingston, THIS JOURNAL, 49, 439 (1927); Beard and Taylor, *ibid.*, 51, 1975 (1929).

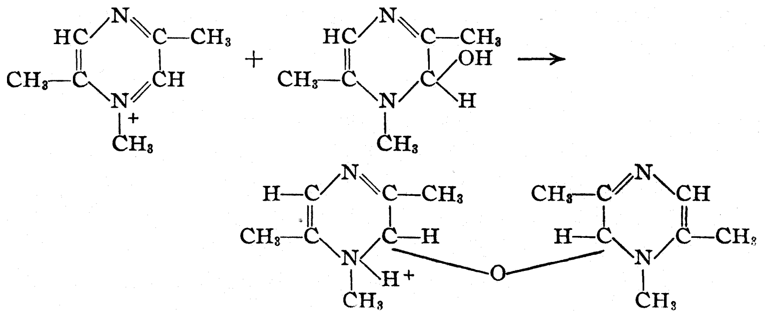
is closer than the accuracy of the extrapolation or that of (5) at such high values of the ionic strength. The data of Table IV are in accord with our assumptions. At the end of this run the values of (OH–), the sodium iodide concentration, and the total salt concentrations are the same as those at the start of the run in Table III. This point is indicated in Fig. **3** by the broken vertical line. The two sets of data fall into the same curve bb at this point. For the run in Table III after 19.5 minutes, when $\mu = 0.01486$, the value of $k'_{\text{iii}} = 43.44$ (calculated from (5) and $k_{\text{iii}} = 57.5$ at $\mu = 0$). From the values $k_3 = 69.9$ and (OH–) $= 0.00715$ at this point, using (4), $k'_{\text{iv}} = 37.1$ X 10^2. By relation (6) k_{iv} at $\mu = 0$ is then calculated to be 65.0 X 10^2. The values of k_3 calcd. in Table III (Col. 6) and Table IV (Col. 7) are calculated from the above values of k_{iii} and k_{iv} at $\mu = 0$ and (OH–) using relations (5), (6) and (4). The agreement with the experimental values is within the experimental error. Further, relations (5) and (6) are limiting relations which, although holding quite well when $\mu < 0.01$, become far from accurate as μ increases. For this reason no values of k_3 calcd. are given for Table II.

Since, from statistical considerations, reaction through triple or quadruple collisions is generally regarded as improbable, reactions (a-1) and (b) must be considered as taking place in two steps, the first step being a rapid equilibrium and the second a dimolecular reaction. It will be assumed that both (a-1) and (b) have the same reversible step



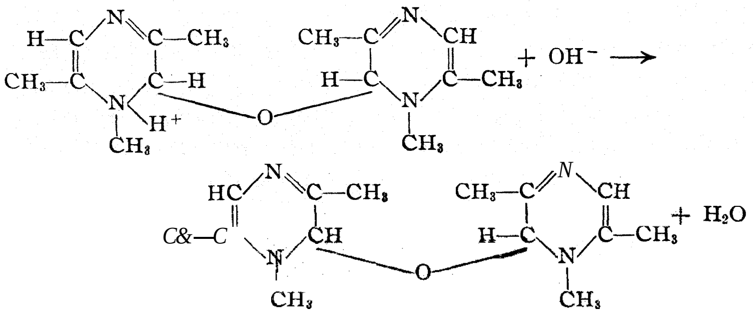
(A)

The initial value of the conductivity points to only very small equilibrium amounts of the pseudo base. Denoting the pseudo base by P – OH, $K_A = (\text{P} - \text{OH})/(\text{Py}^+)(\text{OH}^-)$ is the equilibrium constant of reaction A. If this is followed by the slow reaction



(B-1)

succeeded by the rapid reaction



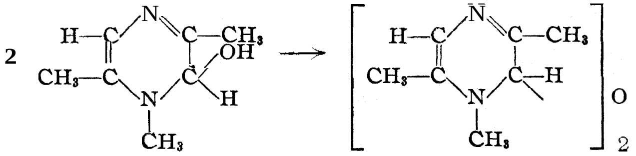
(B-2)

(B-1) therefore controlling the rate of the entire process, then

$$\frac{d(Py^+)}{dt} = k_B(P - OH)(Py^+)$$

$$\frac{d(Py^+)}{dt} = K_A k_B (Py^+)^2(OH^-) = k'_{iii}(Py^+)^2(OH^-).$$

If the slow reaction taking place is



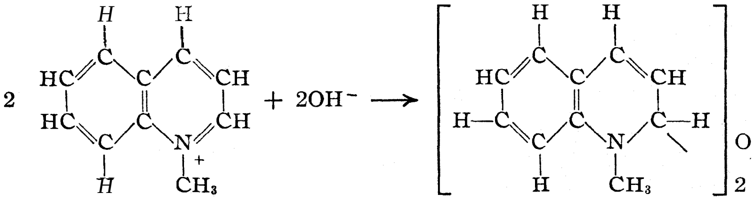
(C)

yielding the same ether as above

$$\frac{d(Py^+)}{dt} = \frac{d(P - OH)}{dt} = k_c(P - OH)^2 = K_A^2 k_c (Py^+)^2(OH^-)^2$$

$$dt \quad = k'_{iv}(Py^+)^2(OH^-)^2.$$

The formation of such ethers is characteristic of pseudo bases in the quinoline series.[14] Hantzsch and Kalb found that such an ether precipitated from dilute solution of N-methylquinolinium hydroxide (*N*/16)



with a corresponding decrease in conductivity.[2] Such ethers yield the salt of the original base upon treatment with acid.[2,15] It has been shown that the final product obtained in the above reactions can be changed back into the original pyrazinium salt by the addition of acid. A run was made using the same concentrations as that in Table II in which 25

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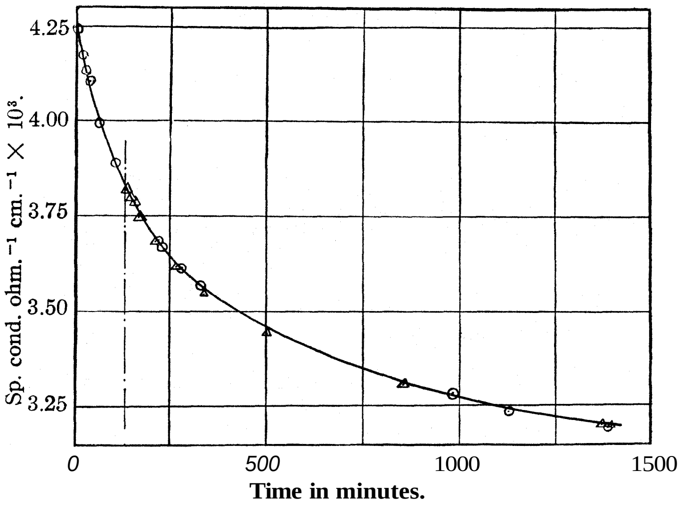
[14] La Coste, *Ber.*, 15, 189 (1882).

[15] Decker, *ibid.*, 35. 3073 (1902).

cc. of 0.06237 N sodium hydroxide and 25 cc. of 0.06237 N 1,2,5-trimethylpyrazinium iodide were allowed to react for 307 minutes (83.6% completion) in the absence of oxygen, at 25.00'; 50 cc. of 0.06268 N hydrochloric acid was then added and the mixture allowed to stand for six days at 25.00'; 25 cc. of this mixture was then mixed with 25.0 cc. of 0.03128 N sodium hydroxide at 25.11° in the apparatus of Fig. 1. The conductivity of the solution was followed and compared with that of a blank, using exactly the same quantities but adding the 0.06268 N hydrochloric acid before the original sodium hydroxide, and thus preventing the original reaction. The values of the specific conductance at various times after mixing are shown in Fig. 4 for both runs. The zero time for the blank run is at zero, that for the reversed run is indicated by the broken vertical line at 130 minutes, the time scales being the same. Both sets of data are thus seen to lie on the same curve. The results show that 72.8% of the original salt was present after reversal; that is, that 67.5% of the reacted 1,2,5-trimethylpyrazinium iodide had been regenerated.



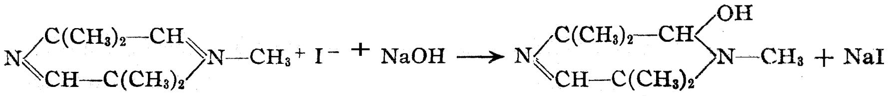
⊙, Blank; A, reversed run.

Fig. 4.—Specific conductances in reversed and blank runs

An attempt to isolate this ether, described in the previous paper, resulted in a product which decomposed so rapidly that analytical evidence as to its nature was meaningless. Its reactions are now being studied.

The reactions B and C above present certain analogies with hemiacetal and acetal formation, respectively. Such reactions are known to occur simultaneously.

The Reaction between 1,2,2,5,5-Pentamethyldihydropyrazinium Iodide and Sodium Hydroxide in Water at 0°.—A preliminary study of this reaction by the method just described showed that the changes were too rapid to measure both at 25 and 0°. When equivalent quantities of the two solutions were mixed the conductivity of the solution was 14% greater than that calculated for a concentration of sodium iodide,[16] corresponding to that formed in the reaction

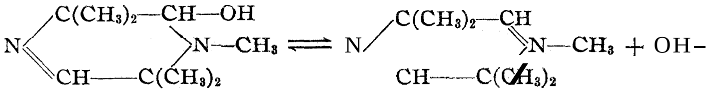

Pseudo base

which has already been shown to take place by the isolation of the pseudo base.[1]

Ten cc. of 0.01092 N sodium hydroxide was mixed with 10 cc. of 0.01092 *N* 1,2,2,5,5-pentamethyldihydropyrazinium iodide (specific conductance 5.59×10^{-4} ohm^{-1} cm.$^{-1}$ at 0°. The observed specific conductance of the solution immediately after mixing at 0° was 4.06×10^{-4} ohm^{-1} cm.$^{-1}$ calculated for 0.00546 N NaI at 0°, 3.57×10^{-4} ohm^{-1} cm.$^{-1}$; diff. due to base, 0.49×10^{-4}).[17]

A value of the limiting equivalent conductance at 25.00° $\Lambda_0 = 109.6$ for 1,2,2,5,5-pentamethyldihydropyrazinium iodide was calculated approximately from $\Lambda = 97.6$ at 0.01092 N, measured at 25.00°, assuming $\Lambda/\Lambda_0 = 0.89$ (the value for 1,2,5-trimethylpyrazinium iodide at the same concentration). For 1,2,2,5,5-pentamethyldihydropyrazinium hydroxide $\Lambda_0 = 226.9$ at 25.00° calculated from Λ_0 for the iodide and the limiting equivalent conductances $\Lambda_{0OH^-} = 192.7$ $\Lambda_{0I^-} = 76.5$ at 25.00°.

Below are given values of K for the equilibrium



calculated from conductance measurements on 1,2,2,5,5-pentamethyl-6-hydroxytetrahydropyrazine, using the relationship $K = (\Lambda/\Lambda_0)^2C/(1 - \Lambda/\Lambda_0)$, taking $\Lambda_0 = 226.9$ as found above.

TABLE V

EXPERIMENTAL DATA

Concn. eqts./liter	Specific conductance ohm^{-1} cm.$^{-1}$ $\times 10^5$	Λ	Λ/Λ_0	$K \times 10^6$
0.00589	6.21	10.6	0.0466	1.34
.01100	7.59	6.9	.0303	1.34

The values of the specific conductance taken within fifteen minutes of mixing increased 60% on standing for twenty-four hours. They are in rough agreement with the difference obtained above at 0° (0.49×10^{-4}

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[16] Compare Stewart and Maeser, THIS JOURNAL, 46, 2583 (1924).

[17] From the data of Jones, "International Critical Tables," Vol. VI, p. 235.

ohm^{-1} cm.$^{-1}$ due to 0.005 N solution of the base). These values of K are probably much too high for the pseudo basic system which, in the previous paper, was shown to be a weaker base than the unmethylated nitrogen, to which therefore a large part of the conductivity must be due. The complete stability of the base in water for intervals of at least an hour was shown in the previous paper and therefore these results indicate that the equilibrium between 1,2,2,5,5-pentamethyldihydropyrazinium hydroxide and 1,2,2,5,5-pentamethyl-6-hydroxytetrahydropyrazine is established rapidly and greatly favors the latter.

Conductivity of 1,2,2,3,5,5,6-Heptamethyldihydropyrazinium Iodide at 25.00°.—Two Freas conductivity cells with cell constants 0.3496 and 0.3370 were used. The constants were determined using a solution of 0.7476 g. of potassium chloride in 1000 g. of water whose specific conductance was taken as 0.0014104 (the Kohlrausch value corrected to the standards of Parker and Parker).[18] The results are given in Table VI. The theoretical equivalent weight of 308.2 was used in the computations. The accuracy is the same as previously.

TABLE VI

CONDUCTIVITY OF 1,2,2,3,5,5,6-HEPTAMETHYLDIHYDROPYRAZINIUM IODIDE AT 25.00°

G. per liter	Specific conductance, ohm^{-1} cm.$^{-1}$ × 10^3	Concn. eqts. per liter × 10^2	Λ	$\frac{\Lambda}{\alpha \text{ std.}}$[a]
3.438	1.0343	1.1155	92.8	104.4
3.387	1.0148	1.0985	92.5	103.9
1.695	0.5283	0.5500	96.1	104.5
0.8468	.2708	.2748	98.5	104.5
.8465	.2694	.2746	98.2	104.2
.4230	.1386	.1372	101.1	105.4
	Extrapolated	0	104.7	104.7

[a] α std. = Λ/Λ_0 for 1,2,5-trimethylpyrazinium hydroxide.

The value of Λ_0 was obtained using the extrapolation method of Randall. From $\Lambda_{0\,I^-} = 76.9$ and $\Lambda_{0\,OH^-} = 194.0$,[19] the limiting equivalent conductance of 1,2,2,5,5,6-heptamethyldihydropyrazinium hydroxide at 25.00° was calculated to be $\Lambda_0 = 222.0 \pm 1\%$.

The Reaction between 1,2,2,3,5,5,6-Heptamethyldihydropyrazinium Iodide and Sodium Hydroxide in Water at 25.00°.—This reaction was studied using the same Freas cells at 25.00 ± 0.05°. 10 cc. of the solution of the pyrazinium salt was allowed to come to temperature in the thermostat; 10 cc. of the sodium hydroxide solution, withdrawn from the thermostat, was then introduced into the cell by a pipet and the contents of the

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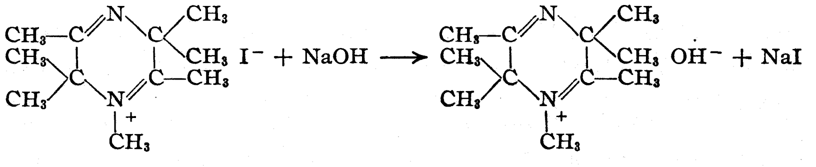
[18] "International Critical Tables," Vol. VI, p. 230.

[19] Calculated from data in "International Critical Tables," Vol. VI, p. 230, $\Lambda_{0\,OH^-}$ being somewhat weighted by comparison with a value calculated from the data of Randall on sodium hydroxide.

cell mixed by thorough shaking in the thermostat. The temperature in the cell immediately after mixing, by actual test, was never more than 0.1" above that of the thermostat, due to the transference of the sodium hydroxide. The conductivity of the solution was measured as soon as possible after mixing. The specific conductances of certain mixtures at various time intervals are given in Col. 2, Tables VIII, IX, X and XI, the times being given in Col. 1. To save space only a few of the values are given for each run. The zero time values were obtained by extrapolation. Times were measured as before. The fall in conductivity is due to the slow production of a weaker base, whose dissociation was shown to be negligible from the final conductivity of the reaction mixture. For the runs using equal quantities the initial specific conductance due to the base was obtained from the extrapolated zero time values of the specific conductance by subtracting the estimated specific conductance due to the sodium iodide assuming that the metathesis reaction


(A)

takes place completely. For the runs where excess of the dihydropyrazinium iodide was present the estimated specific conductance of this excess was also subtracted. The values of A for sodium iodide and the dihydropyrazinium iodide used in the calculation were read from plots of Λ against $\sqrt{C}$ and were taken at a concentration equal to the sum of the over-all concentrations of the sodium iodide and dihydropyrazinium iodide plus the concentration of ionized pyrazinium base. A decrease in the mobility of one pair of ions due to the presence of the remaining ions was thus corrected for as far as possible. The data on sodium iodide were from Jones.[20] Assuming that the pyrazinium base yielded the same positive ion as the salt, the limiting equivalent conductance of the base was taken as that of 1,2,2,3,5,5,6-heptamethylpyrazinium hydroxide $\Lambda_0 = 222.0$. This does not allow for a decrease in mobility of the type mentioned above. The error thus introduced is probably not more than 5%. From these results the values of the basic dissociation constants in Table VII were calculated. The concentrations of the pyrazinium base, C_b, pyrazinium iodide, C_{PyI}, and sodium iodide, calculated on the assumption of complete metathesis, are given in Cols. 1, 2 and 3, respectively. Columns 4 and 5 contain, respectively, the total specific conductance and that due to the base. The calculated values of Λ/Λ_0 for the base are given in col. 6. The values of K_B given in Col. 7 are calculated from the relations

[20] "International Critical Tables," Vol. VI, p. 230

$$K_B = \frac{(\Lambda/\Lambda_0)^2 C_b}{1 - \Lambda/\Lambda_0} \quad (1)$$

$$K_B = \frac{\Lambda/\Lambda_0 C_b \,(C_{PyI} + \Lambda/\Lambda_0\, C_b)}{(1 - \Lambda/\Lambda_0)\, C_b} \quad (2)$$

where C_b and C_{PyI} are, respectively, the concentrations of pyrazinium base and iodide. Relation 1 was used when C_{PyI} was zero and relation 2 when the pyrazinium iodide was present.

Table VII

Dissociation Constants at 25.00°

Over-all concn PyOH eqts /liter X 10^3	Concn. PyI eqts./liter X 10^3	Concn. NaI eqts./liter × 10^3	Total sp. cond. ohm-' cm $^{-1}$ × 104	Sp. cond. of base ohm^{-1} cm $^{-1}$ × 10^4	Λ/Λ_0	K_B X 10^3
5.497	0	5.497	13.51	6.89	0.565	4.03
2.745	0	2.745	7.455	4.100	.672	3.78
1.374	0	1.374	3.988	2.293	.752	3.13
2.748	2.748	2.748	8.99	3.060	.502	4.15

In Col. 3, Tables VIII, IX, X and XI, the values of the concentration of pyrazinium base whose dissociation constant is calculated above were estimated from the total specific conductance given in Col. 2 with the aid of graphs prepared for each run as follows: the specific conductance due to rounded concentration of the base was estimated from the Λ/Λ_0 values calculated from K_B appearing at the head of the table using either (1) or (2). The specific conductances, calcuated as above, due to the sodium iodide and to the pyrazinium iodide, when present, were added

Table VIII

Change of Specific Conductance and Calculated Concentrations after Mixing Equal Quantities of 0.01099 N Sodium Hydroxide and 0.01099 *N* 1,2,2,3,5,5,6-Heptamethyldihydropyrazinium Iodide at 25.0° (Three Runs). Kg = 4.1 X 10^{-3}

Time, min.	Specific conductance. ohm $^{-1}$ cm $^{-1}$ X 10^3	Concn PyOH, C_b, eqts /liter X 10^3	$\frac{d\,1/C_b}{dt}$ liter/mol /min.	a	k, min $^{-1}$
0.00	1.351	5.49	..	..	..
2.17	1.338	5.31	..	..	..
4.17	1.328	5.20	..	..	..
5.32	1.320	5.11	..	..	..
12.60	1.289	4.77	2.05	0.592	5.84
27 00	1.236	4 21	2.15	.613	5.73
39.0	1.194	3.78	2.25	.654	5.28
68.7	1.106	2.955	2.45	.674	5.39
83 6	1 076	2.691	2.51	.689	5.40
96.2	1.051	2.477	2.69	.703	5.44
115.7	1.014	2.175	2.78	.723	5.31
133.3	0 989	1.980	2.92	.738	5.36
160.5	.951	1.690	3 04	.762	5.24
189.2	.922	1.485	3.10	.780	5.10
240.3	.875	1.155	3.41	.813	5.16

TABLE IX

CHANGE OF SPECIFIC CONDUCTANCE AND CALCULATED CONCENTRATIONS AFTER MIXING EQUAL QUANTITIES OF 0.0055 *N* SODIUM HYDROXIDE AND 0.0055 *N* 1,2,2,3,5,5,6-HEPTAMETHYLDIHYDROPYRAZINIUM IODIDE AT 25.00°. $K_B = 3.78 \times 10^{-3}$

Time, min.	Specific conductance ohm^{-1} cm.$^{-1}$ X 10^3	Concn. PyOH, C_b eqts./liter X 10^3	$\frac{d\ 1/C_b}{dt}$ liter/mol./min.	α	k, min.$^{-1}$
0	0.7455	2.750	..	..	..
5.1	.7338	2.638	..	..	..
7.25	.7285	2.597	..	..	..
10.00	.7222	2.537	2.79	0.686	5.93
15.2	.7120	2.450	..	..	..
19.9	.7033	2.370	..	..	..
31.1	.6833	2.205	..	..	..
35.5	.6765	2.150	2.95	.713	5.81
55.7	.6465	1.907	3.01	.732	5.61
112.4	.5820	1.428	3.20	.775	5.33
244.1	.4979	0.860	3.75	.840	5.32
246.2	.4969	.854	..	..	..

TABLE X

CHANGE OF SPECIFIC CONDUCTANCE AND CALCULATED CONCENTRATIONS AFTER MIXING EQUAL QUANTITIES OF 0.00275 *N* SODIUM HYDROXIDE AND 0.00275 *N* 1,2,2,3,5,5,6-HEPTAMETHYLDIHYDROPYRAZINIUM IODIDE AT 25.00°. $K_B = 3.13 \times 10^{-3}$

Time, min.	Specific conductance ohm-' cm.$^{-1}$ × 103	Concn. PyOH C_b eqts./liter X 10^3	$\frac{d\ 1/C_b}{dt}$ liter/mol./min.	a	k, min.$^{-1}$
0	0.3988	1.372			
6.75	.3930	1.328	...		
9.75	.3908	1.312	...		
13.6	.3875	1.289	...		
18.0	.3843	1.265	...		..
22.25	.3812	1.243	3.403	0.767	5.82
30.25	.3758	1.204			
42.6	.3678	1.146	...	..	..
54.5	.3601	1.092	3.513	.785	5.70
73.3	.3496	1.020	3.572	.795	5.65
124.5	.3256	0.859	3.608	.812	5.47
160.9	.3118	.770	...	..	
214.4	.2957	.669	3.715	.842	5.24
313.7	.2730	.532			
401.3	.2593	.455			

to that of the base. The values of the total specific conductance thus obtained were plotted against the total concentration of the pyrazinium base.

If the following reaction is responsible for the disappearance of the pyrazinium base, and if, as before, C_b represents the over-all concentration of pyrazinium base, then

$$\text{Py}^{+} + \text{OH}^{-} \longrightarrow \textbf{products}$$

$$\frac{d\,C_b}{dt} = k(\text{Py}^{+})(\text{OH}^{-}) \qquad (3)$$

TABLE XI

CHANGE OF SPECIFIC CONDUCTANCE AND CALCULATED CONCENTRATIONS AFTER MIXING EQUAL QUANTITIES OF 0.00550 *N* SODIUM HYDROXIDE AND 0.01099 *N* 1,2,2,5,5,6-HEPTAMETHYLDIHYDROPYRAZINIUM IODIDE AT 25.00°. $K_B = 4.15 \times 10^{-3}$

Time, min.	Sp. cond. ohm^{-1} cm.$^{-1}$ $\times 10^3$	Concn. PyOH, C_b, eqts./liter $\times 10^3$	$\frac{dC_b}{dt}$ liter/min. $\times 10^2$	(OH$^-$), eqts./liter $\times 10^3$	(Py$^+$), eqts./liter $\times 10^3$	k, min^{-1}
0	0.8990	2.750				
8.2	.8790	2.535	..	...	...	..
11.04	.8715	2.457	2.49	1.251	3.998	4.98
16.00	.8590	2.330	..	...	...	..
19.75	.8510	2.245	2.32	1.157	3.904	5.13
25.90	.8373	2.110	..	...	...	..
29.65	.8293	2.030	2.02	1.085	3.832	4.85
32.75	.8235	1.972	..	...	...	..
35.2	.8185	1.925	..	...	...	..
48.1	.7955	1.697	1.70	0.904	3.651	5.15
67.5	.7665	1.425	1.28	.771	3.518	4.72
96.3	.7315	1.105	..	...	...	..
118.0	.7120	0.932	..	...	...	..

and when no excess of either ion is present

$$\frac{dC_b}{dt} = k(\Lambda/\Lambda_0)^2 C_b^2$$

$$\frac{d\frac{1}{C_b}}{dt} = (\Lambda/\Lambda_0)^2 k = \alpha^2 k \qquad (4)$$

For the runs in Tables VIII, IX and X, where the reactants were in equal concentrations, the values of $1/C_b$ were plotted against t. Such a plot from the data of Table VIII is given in Fig. 5. The slopes of the tangents to these curves are given in Col. 4 of these tables. Column 6 gives the values of k calculated from these slopes using Equation 4, and the values of $a = \Lambda/\Lambda_0$ (Col. 5), calculated from (1) and the value of K_B. For the run in Table XI, where the reactants were not equal, the values of k in Col. 7 were calculated by Equation 3 from the slopes of the tangent to a plot of the concentration of pyrazinium base against time (Col. 4), and the values of $(OH^-) = \Lambda/\Lambda_0 C_b$ and $(Py^+) = \Lambda/\Lambda_0 C_b + 0.002747$ (Cols 5 and 6), $\alpha = \Lambda/\Lambda_0$ being calculated from (2).

The Rate of Disappearance of 1,2,2,3,5,5-Hexamethyl-6-methylenetetrahydropyrazine from its Water Solutions at 25.00°.—This base was obtained as an oil on adding 40% potassium hydroxide to solutions of 1,2,2,3,5,5,6-heptamethyldihydropyrazinium iodide. It was described in the previous paper. A freshly distilled sample (b. p. (6.5 mm.) 78°) was used. Twenty cc. of water in the type of cell used in the previous experiment was allowed to come to equilibrium with the thermostat;

0.0489 g of base was added and the cell shaken. The change in conductivity of the resulting **0.01357** *M* solution was observed as it fell with

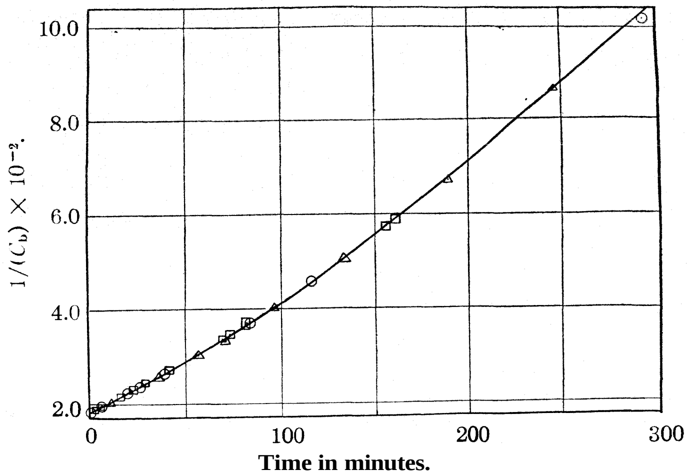


Fig. 5. —Graph from the data of Table VIII: ⊙, El, △, respective points of three runs.

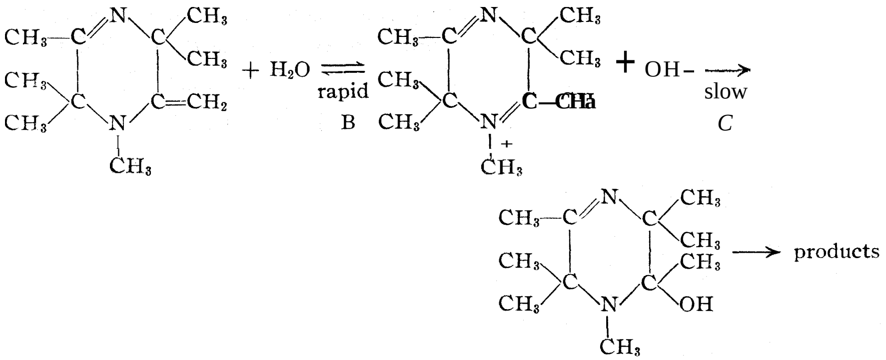
the time. Zero time was taken as that just after shaking. The results are given in Table XII. From the extrapolated zero time value of the

Table XII

Change of Specific Conductance and Calculated Concentrations in a Water Solution of 1,2,2,3,5,5-Hexamethyl-6-methylene-tetrahydropyrazine at 25 00°

Time, min.	Specific conductance ohm^{-1} cm.$^{-1}$ $\times 10^2$	Concn. PyOH, C_b, eqts./liter $\times 10^2$	$\frac{d(1/C_b)}{dt}$ liter/mol/min.	a	k, min.$^{-1}$
0	1.226	1.300	..	..	..
3.25	1.184	1 228	..	..	..
4.83	1.164	1.196	1.36	0.439	7.06
6.71	1.141	1.157	..	..	..
18.75	1.016	0.969	..	..	..
23.75	0.973	.907	1.45	.484	6.19
31.55	.912	.822	..	..	..
36 0	.879	.778	..	..	..
42.3	.8355	.721	..	..	..
55.2	.7570	.625	1.74	.545	5.86
62.9	.7150	.577		..	..
71.9	.6680	.522	1.93	.572	5.89
83.5	.6188	.468	2.02	.595	5.71
90.2	.5920	.440	..	..	..

specific conductance, **1.226** $\times 10^{-2}$ ohm^{-1} cm.$^{-1}$, assuming dissociation into 1,2,2,3,5,5,6-heptamethyldihydropyrazinium and hydroxide ions (*i. e.*, $\Lambda_0 = 222$) a value of K_B for the dissociation B



was calculated. This gave

$$K_B = \frac{(\mathrm{Py}^+)(\mathrm{OH}^-)}{(\text{undissociated base})} = \frac{(\Lambda/\Lambda_0)^2}{1 - \Lambda/\Lambda_0} = 3.79 \times 10^{-3}$$

which compares very favorably with those in Table VII. The difference is probably caused by the uncertainty of the extrapolation due to difficulty in estimating the starting time. The concentrations of the base (C) given in Col. 3, Table XII, are calculated from the specific conductances in Col. 2, assuming $K_B = 4.1 \times 10^{-3}$ (taken from Table VII). Column 6 gives the values of k calculated from the a-values in Col. 5 and the slopes of the tangents to the curve $1/C$ against time (Col. 4), using Equation 4 as was done in Tables VIII to X, with which the results agree quite well.

These results show that on mixing 1,2,2,3,5,5,6-heptamethyldihydropyrazinium iodide with sodium hydroxide, the equilibrium B is rapidly established, giving rise to the same system yielded by dissolving 1,2,2,3,5,5-hexamethyl-6-methyl-tetrahydropyrazine in water. In the previous paper the decrease in basicity of the solution was shown to be accompanied by decomposition. Reversal experiments as in the case of 1,2,5-trimethylpyrazinium hydroxide pointed to decomposition also. The rates show that this decomposition is probably controlled by the rate of formation of the pseudo base from its ions (reaction C above). In support of this view, the strong basicity of the system indicates that equilibrium, with the pseudo base, which, as in the case of 1,2,2,5,5-pentamethyldihydropyrazinium hydroxide, would give rise to a weak base, is not reached. Consequently, as was pointed out in the previous paper, the equilibrium B must be reached through an enolic type of change, not through the pseudo base.

Methylphenylacridinium Hydroxide.—In Fig. 6 is shown a graph of $1/(\Lambda - \Lambda_0)$ against the time where Λ is the total equivalent conductance of the solution at various times after mixing 1/128 N solutions of 5-phenyl-10-methylacridinium chloride and sodium hydroxide at 0° and

Λ_∞ is the equivalent conductance due to sodium chloride at the end of the reaction at 0°.[21] $\Lambda - \Lambda_\infty$ is thus the equivalent conductance of methylphenylacridinium hydroxide. This graph points to a heterogeneous reaction.

5-Phenyl-10-methylacridinium hydroxide (methylphenylacridol) was precipitated from phenylmethylacridinium sulfate with sodium hydroxide and its solubility determined at room temperature (25°) by shaking the base with boiled distilled water. The excess solid was filtered off and an excess of sulfuric acid added. The concentration of phenylmethylacridinium salt in the resulting solution was estimated colorimetrically by comparison with a solution of 5-phenyl-10-methylacridinium sulfate of known concentration containing the same concentration of acid. The original yellow color of the solution of the base did not change in shade or intensity on adding the acid. Since the solid base is colorless, this indicates that the color of the solutions of the salt and base are due to the acridinium ion, and that in the saturated solution the phenylmethylacridinium hydroxide is almost completely ionized. The solubility was found to be 1.25×10^{-4} mole per liter. This value is 3.2% of the concentration responsible for the initial $1/\Lambda - \Lambda_\infty$ value in Fig. 6, which must, therefore, be due to supersaturation. The fall in conductivity is due to precipitation from the supersaturated solution. The value of $\Lambda - \Lambda_\infty$ at equilibrium should, therefore, be less than 3.2% of the initial value, since the solubilities were determined at 25°. The corresponding value of $1/\Lambda - \Lambda_\infty$ is seen to be in agreement with this. It thus appears that the equilibrium in the reaction

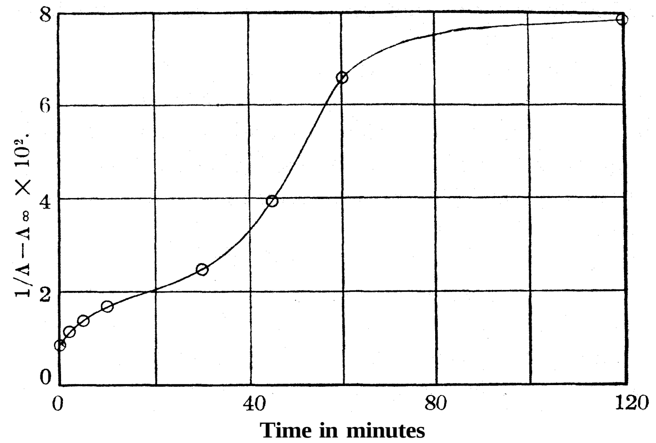


Fig. 6.—Graph of Hantzsch's data on phenylmethylacridinium hydroxide.

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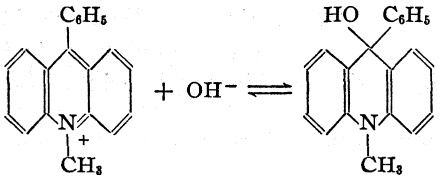
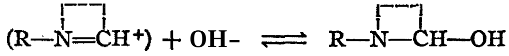
[21] Hantzsch and Kalb, Ref. 2. For convenience these authors' terms are used.



is shifted to the right due to the insolubility of the base, which is largely ionized into the two ions on the left. The rate-controlling step in the measurements of Hantzsch is this rate of crystallization.

Discussion of Results

On the basis of the above results and a reinterpretation of the data of Hantzsch and Kalb, it seems that the position of equilibrium in the reaction



$$(\mathrm{R{-}N{=}CH^+}) + \mathrm{OH^-} \rightleftharpoons \mathrm{R{-}N{-}CH{-}OH}$$

Pseudo base

depends on the conjugation in the ring and the tendency of the N=C double linkage to add OH–. In the case of 1,2,5-trimethylpyrazinium hydroxide and 5-phenyl-10-methylacridinium hydroxide, for example, the equilibrium is to the left.

The experiments of Hantzsch and Kalb[2] and of Decker[22] have demonstrated this to be true also for methylpyridinium, methylquinolinium, and methylisoquinolinium hydroxides. In all of these compounds the ring is completely conjugated. In the quinolinium series the condensation reaction yielding an ether is a general reaction. 1,2,5-Trimethylpyrazinium hydroxide also undergoes this reaction, yielding an ether.

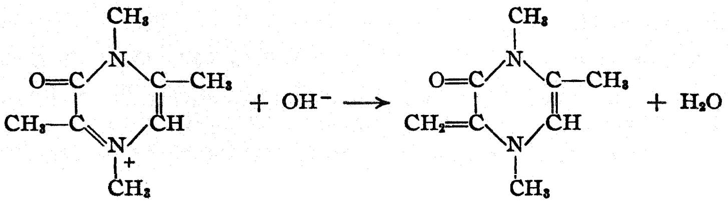
In the case of 1,2,2,5,5-pentamethyldihydropyrazinium hydroxide the double linkage forming part of the pseudo basic system is not conjugated through the ring system, and consequently the double bond has a greater tendency to become saturated by adding OH–. In consequence the equilibrium favors the weakly basic pseudo base.

The rapid equilibrium 1,2,2,3,5,5,6-heptamethyldihydropyrazinium hydroxide with 1,2,2,3,5,5-hexamethyl-6-methylene-tetrahydropyrazine accounts for the apparently weak basicity of the quaternary base (K_B = 4 × 10^{-3}). Such an equilibrium is possible in the case of 1,2,5-trimethylpyrazinium hydroxide but not in the case of 1,2,2,5,5-pentamethyldihydropyrazinium hydroxide. The conjugation in the pyrazinium nucleus probably opposes the reaction in the case 1,2,5-trimethylpyrazinium hydroxide and hence accounts for lack of evidence of a similar equlibrium in this case.

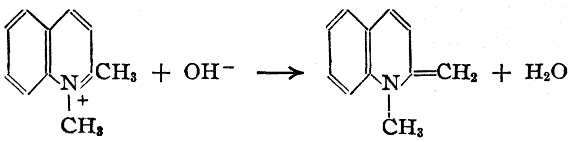
Gastaldi and Princivalle[23] have recently obtained evidence for the reaction

[22] Decker, J. *prakt. Chem.*. 192, 425 (1911).

[23] Gastaldi and Princivalle, *Gazz. chim. ital.*, 59, 791 (1929); 60, 296 (1930); Princivalle, *ibid.*, 60, 298 (1930).



In this case the conjugation in the pyrazine nucleus is also not complete. In this connection, however, it should be mentioned that Konig has obtained 1-methyl-2-methylene-1,2-dihydroquinoline by the action of sodium hydroxide on 1,2-dimethylquinolinium hydroxide[24]



This reaction will be investigated further by the foregoing methods.

Summary

1. The conductivities of 1,2,5-trimethylpyrazinium hydroxide and 1,2,2,5,5-pentamethyldihydropyrazinium hydroxide have been measured at 25°. Their Λ/Λ_0 values are the same at equivalent concentrations and almost the same as those of lithium iodate.

2. The disappearance of strong base from mixtures of 1,2,5-trimethylpyrazinium iodide and sodium hydroxide has been found to take place by two reactions. The one takes place at a rate proportional to the square of the concentration of pyrazinium ion and the first power of the hydroxyl-ion concentration, and the other at a rate proportional to the squares of the concentrations of both of these ions, when allowance is made for a salt effect according to the Brönsted theory. The same primary equilibrium between the quaternary base and the pseudo base hypothesized in both cases is shown to be inappreciably in favor of the pseudo base. Evidence is brought out to show that the final product is the ether of the pseudo base. The similarity between these reactions and those of pseudo bases in the pyridine and quinoline series is discussed.

3. The equilibrium between 1,2,2,5,5-pentamethyldihydropyrazinium hydroxide and 1,2,2,5,5-pentamethyl-6-hydroxytetrahydropyrazine has been found to be in favor of the latter. The equilibrium is established at a rate too rapid to measure even at 0°. The basic dissociation constant of the equilibrium mixture is $K_B < 10^{-5}$.

4. The equilibrium between 1,2,2,3,5,5,6-heptamethyldihydropyrazinium hydroxide and 1,2,2,3,5,5-pentamethyl-6-methylene-tetrahydropyrazine is established at an unmeasurable rate at 25°. The over-all

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[24] König, Ber., 56, 1543 (1923).

base strength of the system is $K_B = 4 \times 10^{-3}$. A decomposition takes place at a rate proportional to the first power of the concentrations of the pyrazinium and hydroxide ions. The rate of formation of the pseudo base is hypothesized as the controlling step in this reaction.

5. The solubility of 5-phenyl-10-methylacridinium hydroxide has been found to be 1×10^{-4} mole/liter at room temperature and solutions of the base appear to be highly ionized. The initial high value of the conductivity on mixing 5-phenyl-10-methylacridinium chloride and sodium hydroxide is shown to be due to supersaturation.

6. The significance of the results is discussed in the light of ring conjugation, which seems to be the determining factor in the quaternary base–pseudo base equilibria.

STATE COLLEGE, PENNSYLVANIA

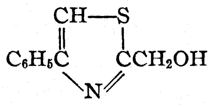
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

SYNTHESIS OF 4-PHENYLTHIAZOLE-2-METHANOL AND SOME OF ITS DERIVATIVES. VIII

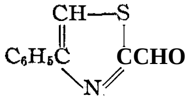
BY JOHN F. OLIN[1] AND TREAT B. JOHNSON

RECEIVED DECEMBER 8, 1930 PUBLISHED APRIL 6, 1931

In the carrying out of our research program dealing with the chemistry of thiazoles, it was necessary to develop practical methods of synthesizing certain thiazoles containing the simplest primary alcohol and an aldehyde group in position 2 of the thiazole ring. The derivatives selected for synthesis were the alcohol and aldehyde of 4-phenylthiazole which are represented by formulas I and II, respectively. These have been prepared by



I



II

methods-which undoubtedly will be of general application for further important syntheses in this series.

The starting points of our research were the thioamides of benzoylglycolic and ethoxyacetic acids, which are represented by formulas III and IV, respectively.

$C_6H_5COOCH_2CSNH_2$ III

$C_2H_5OCH_2CSNH_2$ IV

By interaction of these thioamides III and IV with bromoacetophenone, the benzoate and ethyl ether of the alcohol I are obtained easily in excellent yields. Both derivatives are convertible by hydrolysis into the alcohol I. The benzoate undergoes saponification with alkali easily, while acid hydroly-

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[1] Metz Research Fellow in Organic Chemistry, 1929–1930.

sis with 80% sulfuric acid proved to be the best method for converting the thiazole ether into the alcohol I.

In order to prepare the aldehyde II we applied the usual technique of oxidizing the alcohol in acetic acid solution with chromic acid. This aldehyde II and its precursor the alcohol I are the first representatives of their types to be described in the thiazole series. In the experimental part of this paper are described several derivatives of the alcohol I which are proving to be of immediate service for new synthetic operations now being carried on in our thiazole researches. The work is being continued.

Experimental Part

4-Phenylthiazole-2-methyl Alcohol, C_6H_5T[2]CH_2OH.—The benzoate of this alcohol was prepared as follows. Fifty grams of benzoyl-oxyacetthioamide,[3] 38 g. of bromol acetophenone and 20 cc. of pyridine were dissolved in 100 cc. of alcohol and the solution heated for one hour on a steam-bath. The mixture was then poured into ice water and the insoluble residue washed three times with dilute hydrochloric acid. The benzoate separated and solidified, and was purified by crystallization from 95% alcohol. It separated in the form of rosets melting at 73–74' and the yield was 80% of the theoretical.

Anal. Calcd. for $C_{17}H_{13}O_2NS$: N, 4.74; C, 69.15; H, 4.40. Found: N, 4.52, 4.66; C, 68.95; H, 4.45.

Twenty grams of this benzoate was saponified by warming with potassium hydroxide in alcohol solution. On pouring the hydrolysate into water an oil separated which was extracted with ether, dried over sodium sulfate and finally distilled under diminished pressure. The alcohol boiled at 210–215° at 20 mm. and on cooling solidified immediately. It separated from hot dilute alcohol solution in the form of colorless cubical crystals melting at 88–89°.

Anal. Calcd. for $C_{10}H_9ONS$: N, 7.32; S, 16.77. Found: N, 7.27, 7.45; S, 16.55.

Ethyl Ether of 4-Phenylthiazole-2-methyl Alcohol, $C_6H_5TCH_2OC_2H_5$.—Ethoxyacetonitrile was first prepared according to the method of Gauthier[4] by the action of cuprous cyanide on chloromethyl ethyl ether. The corresponding thioamide was then made by Sommelet's procedure6 and allowed to react in alcohol with the calculated quantity of bromoacetophenone. After two hours of heating on the steam-bath the excess solvent was removed by distillation, the residue washed with dilute sodium hydroxide solution and the thiazole extracted with ether and dried over sodium sulfate. The thiazole ether boiled at 187–188° at 15 mm. and was obtained as an amber-colored oil which is feebly basic. The ether was not altered by digesting with 40% hydrobromic acid solution for four hours.

Anal. Calcd. for $C_{12}H_{13}ONS$: N, 6.39; S, 14.63. Found: N, 6.29, 6.26, 6.30, 6.21; S, 14.51.

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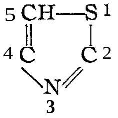
[2] T is the thiazole nucleus.



[3] Olin and Johnson, *Rec. trav. chim.*, *50*, 72 (1931).

[4] Gauthier, *Ann. chim. phys.*, [8] *16*, 302 (1909).

[5] Sommelet, *Compt. rend.*, 142, 828 (1906).

Conversion of the **Ether** into **its** Alcohol.—Fifty grams of the above ether was dissolved in 150 g. of 80% sulfuric acid and the solution heated in an oil-bath at 145–150° for half an hour. The liquid was then poured upon crushed ice and the resulting solution made alkaline with sodium hydroxide. The thiazole separated as an oil and was extracted by ether and purified by distillation. It was obtained in these experiments as a pale yellow, viscous oil which boiled as follows: 210° at 20 mm., 202° at 12 mm. and 178° at 4 mm. The oil solidified on cooling and was purified further by crystallization from dilute alcohol. It separated in the form of cubical crystals melting at 89°. The yield was 65% of the theoretical.

Acetate, $C_6H_5TCH_2OCOCH_3$.—Prepared by heating the thiazole methanol **with** acetic anhydride. It distilled at 193° at 4 mm. and crystallized from petroleum ether in the form of colorless plates melting at 40°.

Anal. Calcd. for $C_{11}H_{11}O_2NS$: N, 6.33. Found: N, 6.15.

Benzoate, **$C_6H_5TCH_2OCOC_6H_5$.—This** is formed by heating the thiazole methanol with benzoyl chloride at 120'. It crystallized from 80% alcohol in the form of rosets melting at 73–74'.

4-Phenylthiazole-2-methyl Bromide, **$C_6H_5TCH_2Br$.—Nineteen** grams of the above methanol was dissolved in 75 cc. of acetic anhydride and hydrogen bromide gas bubbled through the solution, while being warmed on a steam-bath, until saturated. After standing for two hours, the solution was then boiled for forty-five minutes and finally poured into cold water. The bromide separated as an oil. It was washed with sodium carbonate solution, dried in ether over sodium sulfate and finally purified by distillation. It boiled at 195° at 15 mm. The yield was 90% of the theoretical.

Anal. Calcd. for $C_{10}H_8NSBr$: N, 5.51; Br, 31.46. Found: N, 5.38; Br, 31.58.

The corresponding **4-phenylthiazole-2-methyl** chloride, **$C_6H_5TCH_2Cl$**, is easily obtained by the action of phosphorus oxychloride on the thiazole methanol and boils at 184' at 16 mm.

4-Phenylthiazole-2-aldehyde, C_6H_5TCHO.—This is easily obtained by oxidation of the thiazole methanol with sodium dichromate in acetic acid solution. This was accomplished by dissolving 19 g. of the methanol and 20 g. of sodium dichromate in 135 cc. of acetic acid and digesting the mixture at 100° for two hours. After pouring into water and extracting the aldehyde with ether, it was then purified by fractional distillation. It was obtained as a colorless oil possessing a fragrant odor and boiling at 160–162° at 14 mm.

Anal. Calcd. for $C_{10}H_7ONS$: N, 7.40; C, 63.49; H, 3.70. Found: N, 7.48, 7.55, C, 63.37; H, 3.62.

The **phenylhydrazone crystallizes** in canary yellow **prisms** melting at 131–132'.

Anal. Calcd. for $C_{16}H_{13}N_3S$: N, 15.06. Found: N, 15.28.

4-Phenylthiazole-2-aldoin, $C_6H_5TCOCHOHTC_6H_5$.—The above aldehyde behaves normally as an aromatic aldehyde and is converted quantitatively into its aldoin by digestion in alcohol solution in the presence of potassium cyanide. The compound crystallizes from boiling alcohol as yellow needles which turn red on heating and melt at 256°. The compound is insoluble in dilute acids and alkalies and belongs to a new class of compounds corresponding to the benzoins in the benzene series.

Anal. Calcd. for $C_{22}H_{14}O_2N_2S$: N, 7.40. Found: N, 7.40, 7.42.

Summary

1. Methods of synthesizing 4-phenylthiazole-2-methanol and 4-phenylthiazole-2-aldehyde have been described.

2. This alcohol and the aldehyde are the first representatives of their types to be described in the thiazole series.

3. Several derivatives of the thiazole methanol have also been described.

NEW HAVEN, CONNECTICUT

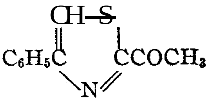
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

SYNTHESIS OF 4-PHENYL-2-ACETOTHIAZOLE. IX

BY JOHN F. OLIN[1] AND TREAT B. JOHNSON

RECEIVED DECEMBER 8, 1930 · PUBLISHED APRIL 6, 1931

So far as the authors are aware, no thiazole ketones have hitherto been described in the chemical literature. Several of the aryl substituted ketone constructions, for example, as represented by the type formulas I and II, have assumed considerable importance in our thiazole researches because they promise to serve as practical starting points for the synthesis of some new types of amino alcohols possessing physiological interest. Such ketone combinations being available, it should then be possible, theoretically, to transform them by an established technique into bridged thiazole amino alcohols having pharmacological properties similar to those of compounds of the adrenaline type. In this paper we now describe a method for preparing the thiazole ketone I.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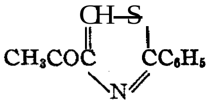
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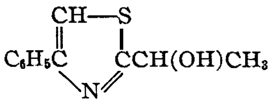
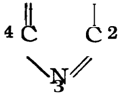

III

The ketone I is easily obtained by oxidation of the thiazole ethanol, III. The latter is a new alcohol which can be prepared easily in quantity by application of a normal thiazole synthesis with bromoacetophenone and the benzoate of lactic-thioamide, which has recently been described by Olin and Johnson.[2] The resulting benzoyl derivative is easily transformed into the alcohol III by the action of alkali. This is the first secondary alcohol of this type to be described in the thiazole series. It is a stable compound and can be oxidized smoothly to the ketone I without destruction of the thiazole ring. This change is accomplished by means of chromic acid in acetic acid solution. The ketone I may be considered as a bridged thiazole ketone corresponding to acetophenone, in which the aryl group is separated from the acetyl radical by the thiazyl nucleus. The ketone exhibits many of the properties of acetophenone and is attacked by bromine in a similar manner with formation of the bromide, $C_6H_5T^*COCH_2Br$.

T* is the thiazyl nucleus



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[1] Metz Research Fellow in Organic Chemistry, 1929–1930.

[2] Olin and Johnson. *Rec. trav. chim.*, 50.72 (1931).

Experimental Part

Benzoate of 4-Phenylthiazole-2-or-ethanol, $C_6H_5TCH(CH_3)OCOC_6H_5$.—Fifty-three grams of benzoyl lactic-thioamide[2] and 50 g. of bromo-acetophenone are dissolved in 150 cc. of alcohol and the solution heated on a steam-bath'for one and one-half hours. Part of the alcohol is then allowed to evaporate and the mixture is made alkaline by the addition of dilute sodium hydroxide solution. The benzoyl thiazole separates as an oil and is extracted by ether and dried over sodium sulfate. The ester was purified by distillation and boiled at 252–254° at 14 mm. Thirty-five grams of a viscous oil was obtained which showed no signs of crystallizing on standing. The thiazole is very feebly basic and possesses a characteristic thiazole odor.

Anal. Calcd. for $C_{18}H_{15}O_2NS$: N, 4.53. Found: N, 4.55, 4.59.

4-Phenylthiazole-2-a-ethanol. 111.—This alcohol is prepared by digesting its corresponding benzoate (above) in alcohol with potassium hydroxide. From 28 g. of the benzoate we obtained 17 g. of the alcohol boiling at 191–194° at 16 mm. It was obtained as an amber-colored viscous oil which solidified on standing. It crystallized from chloroform in the form of large, yellow cubical crystals which melted at 76°. The alcohol is very soluble in all the common organic solvents except petroleum ether, and is insoluble in cold water. Attempts to dehydrate the alcohol by the action of phosphorus pentoxide were unsuccessful. Fifteen grams was digested in benzene with 20 g. of phosphorus pentoxide for fifteen hours without change.

Anal. Calcd. for $C_{11}H_{11}ONS$: N, 6.83; S, 15.61; C, 64.39; H, 5.36. Found: N, 6.80.6.83; S, 15.54; C, 64.20; H, 5.21.

4-Phenyl-2-acetothiazole. I.—Ten grams of the alcohol III is dissolved in 100 cc. of acetic acid and to the solution is added 8 g. of sodium dichromate dissolved in 10 cc of water. After heating this mixture on a steam-bath for one hour, it is poured upon crushed ice, when there is an immediate precipitation of the crude ketone in crystalline condition. It was purified by crystallization from hot dilute alcohol and separated in the form of yellow needles melting at 78–79°. The yield was 9 g. A mixture of this ketone and the alcohol III melted at 55–60". The ketone is much less soluble in the common organic solvents than the alcohol III.

Anal. Calcd. for $C_{11}H_9ONS$: N, 6.89; C, 65.00; H, 4.43. Found: N, 6.75, 6.81; C. 64.91; H, 4.30.

Phenylhydrazone.—Crystallizes in yellow needles melting at 208–209°.

4-Phenyl-2-bromoacetothiazole, $C_6H_5TCOCH_2Br$.—Forty-three grams of the above ketone dissolved in 300 cc. of hot carbon tetrachloride was combined with 34 g. of bromine. There was an immediate reaction with evolution of hydrobromic acid and separation of the hydrobromide of the thiazole. After cooling the mixture and decanting the carbon tetrachloride, the reaction product was triturated with an aqueous solution of potassium hydroxide and the ketone bromide extracted with ether. On evaporating the ether a semi-solid residue was left which dissolved in hot alcohol. On cooling the alcohol solution the above bromide separated in the form of buff-colored needles melting at 106–107°. When the compound was warmed in dilute alkaline solution or with an amine (methylamine), it readily lost its bromine, indicating that the halogen occupies a reactive position in the methyl radical of the ketone group.

Anal. Calcd. for $C_{11}H_8ONSBr$: N, 4.97; Br, 28.3. Found: N, 5.05, 5.07 Br, 27.8.

Summary

1. Benzoyl lactic-thioamide interacts with bromoacetophenone to form the benzoate of 4-phenylthiazole-2-a-tthanol. The corresponding alcohol is obtained by saponification of this ester.

2. 2-Phenylthiazole-2-a-ethanol is oxidized practically quantitatively to the ketone, 4-phenyl-2-acetothiazole, by the action of chromic acid in acetic acid solution.

New Haven, Connecticut

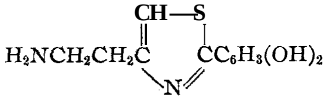
[Contribution from the Department of Chemistry, Yale University]

SYNTHESIS OF SOME NEW THIAZOLE AMINES CONTAINING THE CATECHOL GROUP. X

By John F. Olin[1] and Treat B. Johnson

Received December 8, 1930 Published April 6, 1930

In the first paper of this series Johnson and Gatewood[2] reported the use of chloroacetocatechol as a reagent for thiazole syntheses, and described several thiazoles containing the catechol group in position 4 of the thiazole ring. Suter and Johnson[3] continued the work and described several thiazoles containing the catechol group in both positions 2 and 4 of the thiazole ring. The next contribution to the chemistry of these catechol derivatives was a paper by Hinegardner and Johnson,[4] who described a method of preparing the new thiazole amine represented by formula I.



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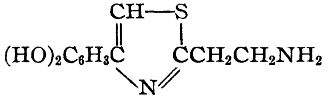

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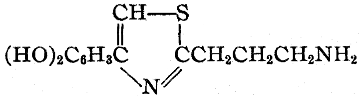

III

This was found to be a potent substance physiologically, and, therefore, it was decided to synthesize its isomer represented by formula II in which the positions of the aliphatic amine and catechol groups in the thiazole nucleus are reversed. It became very important to determine which one of these two amines would be the most active substance when submitted to a comparative pharmacological study. In this paper is described the synthesis of this new thiazole amine II and also its next higher homolog, or the propyl derivative represented by formula III.

Our method of synthesis involved first the preparation of cyanethyl- and cyanpropylphthalimide, second, their conversion into their corresponding thioamides and third, interaction of these respective thioamides with

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[1] Metz Research Fellow in Organic Chemistry, 1929–1930.

[2] Johnson and Gatewood, This Journal, 51, 1815 (1929); U. S. Patent No. 1,743,083 (1930).

[3] Suter and Johnson, This Journal, 52, 1685 (1930).

[4] Hinegardner and Johnson, Paper VI of this series, *ibid.*, 52, 4141 (1930).

chloroacetocatechol to form the phthalimido derivatives of the bases II and III, respectively. Both of these phthalimide compounds can be obtained easily by our method of synthesis in good yields. They are converted almost quantitatively into the amines II and III, respectively, when heated with hydrazine hydrate according to the technique of Ing and Manske.[5] A description of the various stages of our two syntheses is given in the experimental part of this paper.

Experimental Part

γ-Phthalimido-butyrothioamide, $C_6H_4(CO)_2NCH_2CH_2CH_2CSNH_2$.—γ-Chlorobutyronitrile was first prepared by the action of potassium cyanide on trimethylene chlorobromide in alcohol solution.[6] This nitrile was then converted into the phthalimido derivative according to the method of Gabriel[7] by heating it with the potassium salt of phthalimide at 150°. After crystallizing from alcohol, this melted at 81° and the yield was 80% of the theoretical. This nitrile was then converted into its corresponding thioamide by dissolving in alcoholic ammonium sulfide solution and allowing this to stand for seventy-two hours after saturating with hydrogen sulfide. The thioamide crystallizes from 50% alcohol in plates melting at 181–182".

Anal. Calcd. for $C_{12}H_{12}O_2N_2S$: N, 11.29; S, 12.91. Found: N, 11.13, 11.26; S. 12.67.

4-(3,4-Dihydroxyphenyl)-2-γ-phthalimidopropyl-thiazole was prepared by the action of the above thioamide on chloroacetocatechol in alcohol solution. It crystallized from 50% acetone solution in the form of yellow, cubical crystals and melted at 114–115° to an oil.

Anal. Calcd. for $C_{20}H_{16}O_4N_2S \cdot H_2O$: H_2O, 4.52; N, 7.03; S, 8.07. Found: H_2O, 4.22; N. 7.13; S, 8.11.

4-(3,4-Dihydroxyphenyl)-2-γ-aminopropyl-thiazole. III.—The sulfate of this base was prepared as follows. Twenty-five grams of the phthalimide derivative was dissolved in hot alcohol, 6 g. of hydrazine hydrate added and the mixture warmed at boiling water-bath temperature until the solvent evaporated. Dilute hydrochloric acid was then added and the mixture heated to boiling, when phthalylhydrazine separated. After filtering and making the solution alkaline, the above thiazole amine separated. After washing with cold water this was then dissolved in 50% alcohol, acidified with sulfuric acid. On cooling, the sulfate separated in the form of needles. On recrystallizing from hot water this deposited in the form of minute colorless needles resembling very much the crystalline appearance of quinine sulfate. A sample of this salt was dried at 107°, when it lost 16.73% of its weight, indicating a hydrate constitution corresponding to the formula $2C_{12}H_{14}O_2N_2S \cdot 2H_2SO_4 \cdot 7H_2O$. This hydrate melted at 120–140° with decomposition when heated in a closed tube. The anhydrous salt melts at 226–228' to a clear liquid.

Anal. Calcd. for $C_{12}H_{14}O_2N_2S \cdot H_2SO_4$: N, 8.04; S as sulfate, 9.20; total S, 18.41. Found: N, 8.01; S as sulfate, 9.28; total S, 18.61.

Preparation of **4-(3,4-Dihydroxyphenyl)-2-β-aminoethyl-thiazole. II.**—β-Chloropropionitrile was first prepared as follows: 200 g. of thionyl chloride and 100 cc. of chloroform were mixed in a 1-liter two-necked flask to which an Allihn condenser and a

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Ing and Manske, J. *Chem. Soc.*, 128, 2348 (1926).

[6] Henry, *Bull. soc. chim.*, 45, 341 (1886).

[7] Gabriel, *Ber.*, 22, 3335 (1889).

dropping funnel were attached. The end of the dropping funnel tube was drawn out to a capillary ending and arranged so as to approach about one inch above the surface of the chloroform–thionyl chloride solution. One hundred and ten grams of ethylene-cyanhydrin was then added to the boiling chloroform–thionyl chloride solution at the rate of about 3 cc. per minute and the final reaction mixture refluxed for thirty minutes. The chloropropionitrile was separated by fractional distillation under diminished pressure and different preparations were observed to boil as follows: (a) 84° at 30 mm., (b) 80° at 25 mm., 76° at 20 mm. The yield was 127 g. or 91% of the theoretical. Our product always contained a trace of thionyl chloride which could not be removed easily by distillation. By shaking the chloride with dilute sodium carbonate solution the thionyl chloride is removed easily, giving a pure colorless nitrile.

Phthalimido-propionitrile.—This is prepared by heating the above chloride with the potassium salt of phthalimide at 145°. The phthalimide crystallized from methyl alcohol in plates melting at 147–148°. The yield here is greatly reduced by the formation of acrylic nitrile, which is always produced during the fusion with potassium phthalimide.

Anal. Calcd. for $C_{11}H_8O_2N_2$: N, 14.00. Found: N, 14.12, 14.20.

Phthalimido-propionic-thioamide.—This was prepared by heating the above nitrile with an excess of alcoholic ammonium sulfide in a bomb tube at 90°. It crystallized from a mixture of chloroform and absolute alcohol in the form of rosets melting at 187–189°. The yield was good.

Anal. Calcd. for $C_{11}H_{10}O_2N_2S$: N, 11.96; S, 13.69. Found: N, 11.72, 11.85; S, 13.54.

4-(3,4-Dihydroxyphenyl)-2-β-phthalimidoethyl-thiazole.—The above thioamide and chloroacetocatechol interacted smoothly in alcohol solution After warming for thirty minutes at the boiling water-bath temperature this new thiazole separated and was obtained in a crystalline condition after treating the crude reaction product with dilute sodium carbonate solution. It was purified by crystallization from boiling alcohol and separated, on cooling, in the form of needles melting at 203–205°.

Anal, Calcd. for $C_{19}H_{14}O_4N_2S$: N, 7.65; S, 8.75. Found: N, 7.58, 7.53; S, 8.63.

Sulfate of 4-(3,4-Dihydroxyphenyl)-2-β-aminoethyl-thiazole. 11.—The above phthalimide compound was dissolved in hot alcohol and the theoretical quantity of hydrazine hydrate added to the solution. On evaporating the solvent, the reaction product was treated with dilute hydrochloric acid and the insoluble phthalylhydrazide separated by filtration. The hot acid filtrate of the thiazole amine was then mixed with a slight excess of dilute sulfuric acid, when the sulfate of the amine separated immediately in the form of colorless needles.

Anal. Calcd. for $C_{11}H_{12}O_2N_2S{\cdot}H_2SO_4$: N, 8.38; S, as sulfate, 9.59; total S, 19.19; C, 39.52; H, 4.19. Found: N, 8.27; S as sulfate, 9.64; total S, 19.37; C, 39.33; H, 4.05.

Summary

1. In this paper are described methods of synthesizing the two bridged thiazole amines, namely, 4-(3,4-dihydroxyphenylthiazole)-2-β-ethylamine and 4-(3,4-dihydroxyphenylthiazole)2-γ-propylamine.

2. The pharmacological study of both of these amines is now in progress.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

NITRIDATION STUDIES.
III. PHENYL IODIDE DICHLORIDE AND THE N-CHLORO ACID AMIDES AS NITRIDIZING AGENTS[1]

BY A. LAURENCE CURL AND W. CONARD FERNELIUS

RECEIVED DECEMBER 8, 1930 PUBLISHED APRIL 6, 1931

In the development of Franklin's ammonia system of compounds, attention has been directed largely to reactions of double decomposition and to the existence of nitrogen analogs of the familiar oxygen acids, bases, and salts. in the field of inorganic chemistry, and to nitrogen alcohols, aldehydes, etc., among the carbon compounds. Recently, attention has been directed to the oxidation–reduction type of reaction. There is available for liquid ammonia work perhaps the best reducing agent known —a solution of an alkali metal in that solvent—and much work has been and is being carried out using this reagent.[2] The reverse process for nitrogen compounds, nitridation,[3] as it has been called, has not been so thoroughly studied, and only a few nitridizing agents are known.[4] The present investigation had for its purpose the examination of several substances for nitridizing power.

The main requirements of a good nitridizing agent aside from its ease of preparation and purification are: first, that it be of such a nature as to permit its ready and quantitative introduction into a liquid ammonia solution and, second, that its reactivity be such that it does not react with ammonia more readily than with substances in solution in that solvent. Of all substances so far examined, iodine is the most satisfactory although, even with this reagent, special precautions must be taken when introducing it into liquid ammonia.[5] The reactivity of the elements chlorine and bromine toward both gaseous and liquid ammonia is so great as to render

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[1] The material presented in this paper is an abstract of a portion of a thesis submitted by A. Laurence Curl in partial fulfilment of the requirements for the degree of Master of Science at The Ohio State University. The major portion of this material was presented at the 79th meeting of the American Chemical Society, Atlanta, Georgia, April, 1930.

[2] For bibliography see Johnson and Fernelius, J. Chem. *Education*, 6, 20–35 (1929).

[3] The term nitridizing agent was first employed by Turrentine [THIS JOURNAL, 34, 386 (1912)] to describe substances which although they contain no oxygen are nevertheless capable of reacting in a fashion essentially similar to an oxidizing agent. Browne [*ibid.*, 33, 1728 (1911)] and Franklin [J. Phys. Chem., 27, 169 (1923)] applied the term "nitridation" to all those reactions which for the ammonia system of compounds are essentially similar to oxidation reactions for the familiar water compounds. Although nitridation reactions are today classed under the broader conception of oxidation reactions, the newer term does have its use in a specific sense.

[4] For bibliography of nitridation reactions see Schurman and Fernelius, THIS JOURNAL, 52, 2425 (1930).

[5] Ref. 4, p. 2428.

these elements almost useless in the present connection. A halogen may, however, as the present investigation shows, be introduced into liquid ammonia solutions in the form of an addition compound, such as phenyl iodide dichloride, $C_6H_5ICl_2$, which is less reactive toward ammonia than the elementary halogen.

When phenyl iodide dichloride is added to a solution of hydrazobenzene in liquid ammonia at its boiling point, red azobenzene precipitates. The reaction probably takes place as represented by the equation

$$C_6H_5ICl_2 + C_6H_5NH{\cdot}NHC_6H_5 + 2NH_3 \longrightarrow C_6H_5I + 2NH_4Cl + C_6H_5N{=}NC_6H_5$$

although a portion of the dichloride reacts directly with the liquid ammonia. Phenyl iodide dichloride reacts vigorously with both gaseous and liquid ammonia, in accordance with the equation

$$3C_6H_5ICl_2 + 8NH_3 \longrightarrow 3C_6H_5I + N_2 + 6NH_4Cl$$

iodine chloride, ICl, also precipitates azobenzene when added to an open Dewar test-tube containing a liquid ammonia solution of hydrazobenzene.

The oxidizing power of substances containing chlorine in a positive valence state and attached to nitrogen is well known.[6] It was felt that such compounds might be used in a similar capacity in liquid ammonia. However, dichloramine-T, N-chloroacetanilide and N-chlorosuccinimide react so readily with liquid ammonia that they nitridize it preferentially to any hydrazobenzene which may be in solution. Hence these compounds are useless as nitridizing agents. The reaction of the N-chloro acid amides with ammonia, both liquid and gaseous, may be summarized in the equations[7]

$$3\ p\text{-}CH_3C_6H_4SO_2NCl_2 + 10NH_3 \longrightarrow 3\ p\text{-}CH_3C_6H_4SO_2NH_2 + 2N_2 + 6NH_4Cl$$
$$3(CH_2CO)_2NCl + 5NH_3 \longrightarrow 3(CH_2CO)_2NH + N_2 + 3NH_4Cl$$

Such reactions are frequently so vigorous and evolve so much heat that a part of the reacting halogen compound is destroyed.

Chloramine-T is much less reactive than the other compounds. The hydrated compound reacts slowly with gaseous ammonia at room temperature while the anhydrous compound reacts very slowly or not at all. On gentle warming (50°) the hydrated compound reacts more rapidly while the anhydrous form gives a very mild explosion with the formation of a white cloud and a carbonized residue. Both the hydrated and anhydrous forms of chloramine-T go quietly into solution in liquid ammonia and *p*-toluenesulfonamide remains after evaporation of the ammonia. Chlor-

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[6] Hofmann, *Ber.*, 15, 410 (1882); Seliwanow, *ibid.*, 25, 3618 (1892); Lengfeld and Stieglitz, *Am. Chem. J.*, 15, 216 (1893); Chattaway, *J. Chem. Soc.*, *87*, 145 (1905).

[7] Hoogewerff and Van Dorp [*Rec. trav. chim.*, *6*, 381 (1887)] state that potassium benzene sulfonebromoamide reacts with ammonium hydroxide to form the parent amide and a colorless gas. Similarly ammonium hydroxide reacts with N-bromosuccinimide [Lengfeld and Stieglitz, Ref. 6] and chloramine-T [Engfeldt, *Z. physiol. Chem.*, 126, 24 (1923)] to liberate nitrogen. Gebauer-Fiilnegg and Jusa [*Monatsh.*, 50, 65 (1928)] obtained benzene sulfonanilide by adding benzene sulfonechloroanilide to liquid ammonia.

amine-T does not nitridize a liquid ammonia solution of hydrazobenzene at room temperature even in acid solution.[8]

In order to test further the oxidizing (dehydrogenating) properties of both phenyl iodide dichloride and the N-chloro acid amides, the reaction of each of the above substances with hydrazobenzene in chloroform solution was studied. In each case azobenzene and benzidine resulted. The reactions may be summarized

$$C_6H_5ICl_2 + C_6H_5NHNHC_6H_5 \longrightarrow C_6H_5I + C_6H_5N{=}NC_6H_5 + 2HCl$$

$$2(CH_2CO)_2NCl + C_6H_5NHNHC_6H_5 \longrightarrow 2(CH_2CO)_2NH + C_6H_5N{=}NC_6H_5 + 2HCl$$

$$CH_3C_6H_4SO_2NCl_2 + C_6H_5NHNHC_6H_5 \longrightarrow CH_3C_6H_4SO_2NH_2 + C_6H_5N{=}NC_6H_5 + 2HCl$$

$$C_6H_5NHNHC_6H_5 + 2HCl \longrightarrow H_2NC_6H_4C_6H_4NH_2{\cdot}2HCl$$

It is evident that the hydrogen chloride liberated in the oxidation reaction causes a part of the hydrazobenzene to undergo the benzidine rearrangement.

Experimental

Preparation of Materials.—The hydrazobenzene (m. p. 129") was prepared as described elsewhere,[9] and used within a few days of preparation.

Phenyl iodide dichloride was prepared by conducting a stream of dry chlorine into an ice-cold solution of phenyl iodide in chloroform.[10]

To obtain iodine chloride, a stream of chlorine was passed over a few grams of iodine until the liquid first formed began to solidify. The reaction mixture was then warmed gently to decompose whatever iodine trichloride had formed.[11]

The chloramine-T, dichloramine-T and succinimide (m. p. 123") used in these experiments were Eastman Kodak Co. products.

N-chloroacetanilide was prepared by the method of Slosson[12] by adding a solution of potassium hypochlorite to an ice-cold solution of acetanilide: m. p. 88–90"; Slosson gives 91°.

N-chlorosuccinimide was prepared by the method of Tscherniac,[13] which consists of adding a cold solution of snccinimide in dilute acetic acid to an ice-cold solution of potassium hypochlorite: m. p. 149°; Tscherniac gives 150°.

Action upon Hydrazobenzene in Liquid Ammonia. Phenyl Iodide Dichloride.—Using a technique previously described: a solution of 1 g. of hydrazobenzene in liquid ammonia at −33° was treated with 1.53 g. (1.03 equivalents) of phenyl iodide dichloride. A vigorous reaction ensued, resulting in the evolution of a gas and the formation of a red precipitate. Upon evaporation of the ammonia, the reaction products were treated with ligroin. After evaporating the ligroin, a red liquid remained which crystallized on cooling; m. p. 65–67°.

The ligroin insoluble residue was washed with water and the filtrate shown to con-

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[8] Chloramine-T has been found to be more reactive when in an acid solution [Schiemann and Novák, *Z. angew.* Chem., 40,1032 (1927)].

[9] Ref. 4, p. 2428.

[10] Gattermann, "Practical Methods of Organic Chemistry," 3d American ed. from 11th German ed., translated by Schober and Babasinian, The Macmillan Co., New York, 1928, p. 245; *cf.* Willgerodt, *J. prakt. Chem.*, [2]33, **154** (1886).

[11] Gay-Lussac, *Ann. chim.*, **91,** 48 (1814); Bornemann, *Ann.*, 189, 183 (1877).

[12] Slosson, Am. Chem. *J.*, 29,299 (1903).

[13] Tscherniac, *Ber.*, 34, 4213 (1901).

tain ammonium chloride. A light brown substance remained behind (m. p. 115–123°; mixed m. p. with hydrazobenzene 117–120°) in an amount roughly half that of the azobenzene formed.

Iodine Chloride.—Upon adding iodine chloride to a solution of hydrazobenzene in liquid ammonia contained in an open Dewar, a red precipitate formed immediately. After the ammonia had evaporated the residue was washed with ligroin. Upon evaporating the red ligroin solution a red liquid remained which crystallized on cooling; m. p. 58°, mixed melting point with azobenzene 61–63°.

Chloramine-T, N-chloroacetanilide, N-chlorosuccinimide and dichloramine-T failed to give a precipitate of azobenzene when added to liquid ammonia solutions of hydrazobenzene at $-33°$.

Chloramine-T in the presence of ammonium chloride likewise produced no azobenzene at room temperature over a period of nine days.[14]

Action upon Liquid Ammonia. Phenyl Iodide Dichloride.—Upon adding phenyl iodide dichloride in small portions to liquid ammonia, a gentle evolution of gas took place on each addition. A white solid and brown liquid remained after the evaporation of the ammonia. The white solid dissolved in water leaving the brown liquid, which had the odor of phenyl iodide, as a lower layer. The aqueous solution gave tests for ammonium and chloride ions—no iodide. The brown liquid was dissolved in chloroform and treated with chlorine. On standing yellow needles similar to phenyl iodide dichloride deposited.

Two samples of phenyl iodide dichloride, 0.650 g. and 0.769 g., were added to liquid ammonia as above. After evaporation of the ammonia, the residue was washed with ligroin, removed almost quantitatively, filtered and dried in a current of air. Ammonium chloride obtained: 0.240 g. and 0.288 g.; yields based on the equation, $3C_6H_5ICl_2 + 8NH_3 \longrightarrow 3C_6H_5I + N_2 + 6NH_4Cl$: 94.9 and 96.2%.

Chloramine-T.—Both the hydrated and anhydrous forms of chloramine-T dissolved quietly in liquid ammonia. The residues remaining after evaporation of the ammonia were thoroughly washed with water and dried: m. p. 135–136 and 136.0–136.5°, respectively (p-toluenesulfonamide, 137°).

Dichloramine-T, N-chloroacetanilide and N-chlorosuccinimide reacted vigorously with liquid ammonia. The residues remaining after evaporation of the ammonia were shown to consist of ammonium chloride and the respective amide: m. p. 134–136, 113–114 and 120–124°, respectively; mixed melting point of the two latter substances with acetanilide and succinimide, respectively, 113–114 and 121–123°. The *p*-toluenesulfonamide from dichloramine-T was further identified by its solubility in a potassium hydroxide solution.

Action upon Gaseous Ammonia.—The reaction of all of these substances except chloramine-T with gaseous ammonia was vigorous, producing white fumes and a brown and white residue, The reaction of dichloramine-T was so vigorous as to evolve both heat and light. The reaction of hydrated chloramine-T was very slow and attended only by a frothing of the solid. Anhydrous chloramine-T appeared to react not at all with gaseous ammonia at room temperature. Upon warming to 50° in a current of ammonia, there resulted a very mild detonation with considerable increase in pressure and the formation of a white cloud. A tarry charred mass remained behind. Determinations of the nitrogen evolved in these reactions were discouraging. Only in the case of phenyl iodide dichloride is the yield of nitrogen approximately quantitative and seldom did two runs on the same substance check.

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[14] Hydrazobenzene in liquid ammonia solution in the presence of ammonium chloride (an acid in liquid ammonia) is not converted to benzidine over a space of twenty-four days at room temperature.

Action upon Hydrazobenzene in Chloroform Solution.—For these experiments a solution of **2–5 g.** of hydrazobenzene in **50** ml. of chloroform was immersed in an ice-bath and a solution of an equivalent amount of the halogen compound in cold chloroform added slowly with stirring. In each case the color of the solution changed from yellow to red and a precipitate collected at the surface of the chloroform. These precipitates were filtered off, washed with chloroform, dried and dissolved in water. The resulting solutions were neutralized with potassium hydroxide and the brown precipitate resulting recrystallized from hot water. The filtrates were evaporated to dryness and the residues washed with ligroin to remove azobenzene.

	Benzidine		Azobenzene		N-Compd	
Substance	M. p., °C.	Mixed m. p., °C	M. p., °C.	Mixed m. p., °C	M. p., °C	Mixed m. p., °C
Phenyl iodide dichloride	Insufficient		68	68	...	....
Dichloramine-T	115	121–124	62–66	63–67	120–123	131–133
N-Chloroacetanilide	101	115–120	64–67	66–68	113	113–114
N-Chlorosuccinimide	Insufficient		58-65	64-67	114–119	121–124

Summary

1. Phenyl iodide dichloride and iodine chloride may be used as nitridizing agents in liquid ammonia but the N-chloro acid amides so far investigated are valueless in this connection.

2. Phenyl iodide dichloride reacts with ammonia, either liquid or gaseous, to give nitrogen, phenyl iodide and ammonium chloride.

3. The N-chloro acid amides react with ammonia to give the parent amides, ammonium chloride, nitrogen and under certain conditions, tarry decomposition products.

4. In chloroform solution, phenyl iodide dichloride, dichloramine-T, N-chloroacetanilide, and N-chlorosuccinimide convert hydrazobenzene into a mixture of azobenzene and benzidine hydrochloride.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

ESTERIFICATION WITH THIOLACETIC ACID

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RECEIVED DECEMBER 13, 1930 PUBLISHED APRIL 6, 1931

The relative reactivity of primary, secondary and tertiary alcohols with acid chlorides, hydrochloric acid, and in acetal formation has received considerable attention in the past few years. As early as 1879 N. Menschutkin[1] observed a similar marked influence of the structure of alcohols upon their rates of esterification. He measured the rates with which fourteen widely different alcohols react with acetic acid at 154° in the absence of catalyst, and observed that with the exception of methyl alcohol, primary and secondary alcohols show only slight variation among themselves, while the tertiary alcohols show greater differences but invariably esterify one-tenth to one-twentieth as rapidly as do the

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[1] Menschutkin, **Ann., 195, 334 (1879); 197, 193 (1879).**

secondary alcohols. Arthur Michael[2] has studied the reaction rates of these same alcohols with trichloroacetic acid at 25°. Here there is a marked difference between the esterification rates of primary and secondary alcohols with the reactivity of the tertiary alcohols slightly greater than that of the latter. Recently an attempt has been made by Petrenko-Kritchenko, Bogatsky and Lubman[3] to reconcile these results. As these data are of considerable interest to the present paper they are given in part in Tables I and II. The marked difference in the behavior of secondary and tertiary alcohols observed by Menschutkin is absent in the later results, The constants for trichloroacetic acid on the other hand agree well with those of Michael. In the case of the constants for hydrochloric acid the order is entirely reversed from that of acetic acid, with trichloroacetic acid occupying an intermediate position. The phenyl substituted alcohols bring out these effects even more clearly.

TABLE I

Alcohol	CH_3COOH[a]	CCl_3COOH[b]
Methyl	100	0.0370
Ethyl	70.3	.0068
Dimethylcarbinol	26.5	.00098
Trimethylcarbinol	1.4	.00118

[a] From Menschutkin. Percentage esterified at end of one hour, methyl alcohol taken as the standard. [b] From Michael. First order reaction constants.

TABLE II

Alcohol	CH_3COOH	CCl_3COOH	HCl
Ethyl	0.00417	0.02550	0 0348
Dimethylcarbinol	.00237	.00644	.0477
Trimethylcarbinol	.00212	.00692	.2670
Benzyl	.00244	.00815	.0372
Benzhydrol	.00141	.00127	.6060
Triphenylcarbinol	.00040	.00197	2.8480

In an outstanding contribution to the knowledge of the mechanism of esterification, Reid and his collaborators[4] found that thiolbenzoic acid and a primary alcohol gave hydrogen sulfide and a normal ester, whereas benzoic acid and a primary mercaptan gave water and a thiol ester. Using Henry's hypothesis that an intermediate product is formed, this would suggest that the mercaptan adds H- and C_2H_5S- rather than HS- and C_2H_5-. From analogy it is therefore commonly stated that in esterification the hydroxyl used in the formation of water is furnished by the acid and not by the alcohol. This is undoubtedly true for the cases investigated, but the question at once arises whether this is invariably so, especially

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[2] Michael, *Ber.*, 42, 3157 (1909); 43, 464 (1910).

[3] Petrenko-Kritchenko, Bogatsky and Lubman, *Z. physik. Chem.*, *115*, 289 (1925)

[4] Reid, *Am. Chem. J.*, *43*, 489 (1910); THIS JOURNAL, 37, 1934 (1915); **38,** 2746, 2757 (1916); 39, 1930 (1917).

in view of the great differences shown in the reactivity of primary, secondary and tertiary alcohols.

Purpose of Investigation.—The method used by Reid was of a qualitative rather than a quantitative nature. He reports that hydrogen sulfide was either present or absent. When present it was tentatively assumed that the reaction was entirely of one kind. Considering the following reactions

$$\begin{array}{ll} \text{A} & \text{RCO·SH} + \text{R}'\text{O·H} \longrightarrow \text{RCO·OR}' + \text{H}_2\text{S, and} \\ \text{B} & \text{RCOS·H} + \text{R}'\text{·OH} \longrightarrow \text{RCOS·R}' + \text{H}_2\text{O} \end{array}$$

reaction A may take place to the exclusion of B. However, it is also possible that both may be taking place simultaneously. This can only be determined by following quantitatively the disappearance of the acid and the formation of hydrogen sulfide. Furthermore, if the reaction between thiolacetic acid and ethyl alcohol is found to take place in the proportion of 75% according to reaction *A* and 25% according to *B*, it does not necessarily follow that all alcohols will behave in the same way. It was with the hope of being able to determine the proportions of the two reactions A and B occurring in the esterification of a number of alcohols that this work was undertaken. It was also believed that such information might to some extent explain the apparent anomalies in the reaction rates of various alcohols with several different acids. The reactions selected were the esterification of methyl, ethyl, isopropyl and *tert.*-butyl alcohols and triphenylcarbinol with thiolacetic acid.

Experimental Method

The alcohols were purified by the usual methods, the removal of water being the primary object.

Thiolacetic acid at first offered some difficulty as commercial samples invariably contained considerable quantities of hydrogen sulfide. This is best removed by freezing the sample at about —40°, evacuating and allowing the acid to distil *in vacuo* into a trap surrounded by Dry-ice and ether at —70 to —80°. During this distillation the system was continually evacuated. In this way the hydrogen sulfide was entirely pumped off and the freshly distilled acid showed no test for the dissolved gas. This acid was used immediately as it was found that on prolonged standing unless protected from air and moisture hydrogen sulfide was regenerated.

The solvent used was benzene which had been purified by repeated shakings with concd. sulfuric acid, washed and dried.

2 N solutions of the alcohols and acid in benzene were made, equal quantities mixed and the reaction mixture titrated for the acid present; 10-cc. portions of this reaction mixture were introduced into several small hard glass bulbs by means of a capillary. These bulbs were so constructed as to be of uniform volume and have a maximum capacity of 12–13 cc. They were then frozen with liquid air, evacuated and sealed *in vacuo* by means of the capillary. They were then placed in a steel-jacketed vessel fitted with a reflux condenser into which there was a constant stream of carbon tetrachloride vapor. This ensured an even temperature of 76.7°. From time to time the bulbs were removed, frozen with liquid air, opened at the capillary and immediately connected with the hydrogen sulfide analysis train.

This train consisted of three traps, **A,** B and *C*, kept at −40, −80 and −180°, respectively. Trap *C* was connected with an oil pump and the whole system continually evacuated. As the bulb approached room temperature the reaction mixture rapidly distilled into trap A where it again solidified. The sublimation from A to B required a much longer time, but the advantage of passing from one solid phase to another without liquefying permitted the absolute separation of the hydrogen sulfide from the reaction mixture. Trap B then contained the acid–alcohol–benzene mixture which after warming was pipetted out and titrated for the acid present. Trap *C* containing the solid hydrogen sulfide was then disconnected and attached to an absorption bulb containing an ammoniacal solution of cadmium chloride. As the temperature of C was gradually raised the hydrogen sulfide was evolved and precipitated in the absorption bulb as cadmium sulfide. The whole system was finally blown out with a stream of nitrogen and the cadmium sulfide titrated in acid solution with iodine. **A** number of blanks were run and the data in Table III show the method to be entirely satisfactory for the present purpose. Indeed it can be recommended for the analysis of hydrogen sulfide in the presence of any non-gaseous reducing agent.

TABLE III

ANALYTICAL DATA

The amounts are in terms of milliequivalents present in 10 cc. of benzene solution.

	Reagents		**Recovered**	
H_2S	CH_3COSH	CH_3COOH	H B	**Acid**
1.480			1.450	
1.320			1.319	
1.320			1.284	
	10.101[a]		0.467	9.607
	10.267[a]		.479	9.719
0.665		1.925	.640	1.895
.866		3.052	.842	3.000

[a] Subsequent test proved hydrogen sulfide present in the original thiolacetic acid from which these samples were taken.

In the subsequent tables and drawings the course of the reaction is followed under the heading "Esterification" in terms of the millimoles of acid which reacted in the time *t*. For convenience the per cent. of esterification is given in the third column. If the reaction takes place entirely according to Equation **A** previously given, the millimoles of hydrogen sulfide produced should be equal to the millimoles of acid disappearing. The amount of hydrogen sulfide actually produced is given in column four of the tables and by the broken curves. If both reactions expressed by Equations **A** and B are taking place simultaneously, the millimoles of hydrogen sulfide produced will be less than the millimoles of acid disappearing and the fraction of the acid reacting according to Equation **A** is expressed in per cent. in the last column.

Discussion of Data

The data for methyl and ethyl alcohols presented in Tables IV and V (Figs. 1 and 2) would indicate that the percentage of hydrogen sulfide

TABLE IV

ESTERIFICATION OF ALCOHOLS WITH THIOLACETIC ACID IN BENZENE SOLUTION

Methyl alcohol, 1.00 N; thiolacetic acid, 0 957 N; temperature. 76°C.

Time, hrs.	Esterification		H_2S Produced	
	Millimoles	%	Millimoles	%
20	2 15	22.4	1.72	80.1
40	3 42	35.7	2.65	77.4
60	4.40	46.2	3.12	70.9
80	4.85	50.6	3.44	70 9
100	5.32	55.5	4.50	84 5
120	5.54	57 9	4.52	81.5
			Average	77 6

TABLE V

ESTERIFICATION OF ALCOHOLS

Ethyl alcohol, 1 00 N; thiolacetic acid, 0.965 N; temperature, 76°C.

Time, hrs.	Esterification		H_2S Produced	
	Millimoles	%	Millimoles	%
20	1.69	17 6	1.21	71 6
40	2 37	24.3	1 88	79 3
60	3.07	31.8	2.29	74 6
80	3.60	37 2	2.41	67 0
100	3.99	41.4	2.88	72 2
120	4.27	44.3	3 35	78.4
			Average	78 9

produced per mole of acid esterified is the same within experimental error. These results may also be interpreted as indicating that with primary alcohols about 78% of thiolacetic acid esterifies according to equation A and about 22% according to equation B.

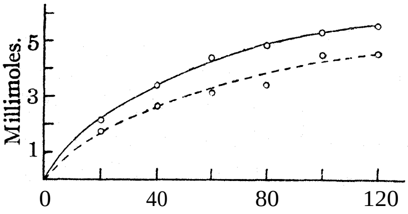


Fig. 1.—Methyl alcohol, 76°: ——, esterification; – – –, H_2S production.

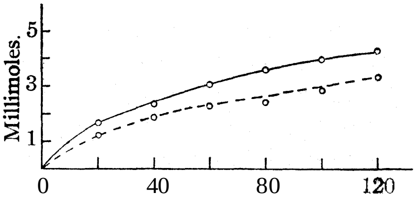


Fig. 2.—Ethyl alcohol, 76°: ——esterification; – – – –, H_2S production.

The behavior of a secondary alcohol, in this case isopropyl, is markedly different, since practically the theoretical quantity, 97.7%, of hydrogen sulfide is produced; Table VI and Fig. 3. It may therefore be assumed that with isopropyl alcohol thiolacetic acid esterifies entirely according to equation A.

As an example of a tertiary aliphatic alcohol the esterification of *tert.*-butyl alcohol was attempted. This reaction is, however, exceedingly

TABLE VI

ESTERIFICATION DATA

Isopropyl alcohol, 1.00 N; thiolacetic acid, 0.952 N; temperature, 76°C.

Time, hrs	Esterification Millimoles	%	H_2S Produced Millimoles	%
40	0.56	5.8	0.55	99.4
60	0.78	8.2	0.76	97.0
80	1.22	12.8	1.22	100.0
100	1.34	14.1	1.28	95.4
120	1.43	15.0	1.38	96.6
			Average	97.7

slow and under prolonged heating was accompanied by decomposition of either the thiolacetic acid or its ester, so that from the data obtained it was impossible to follow the course of the reaction. However, the relative rates of esterification of the secondary and tertiary alcohols are in the same order as obtained by Menschutkin with acetic acid. If possible the velocity constants of the reactions with thiolacetic acid will be investigated.

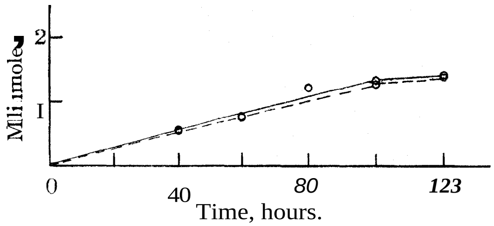


Fig. 3.—Isopropyl alcohol, 76°: ———, esterification; - - - H_2S production.

Triphenylcarbinol, Table VII, and Fig. 4, offers an interesting contrast. Since the reaction was found to proceed too slowly at 76° it was carried out at 100°. As will be shown later at this temperature the acid slowly hydrolyzes to produce hydrogen sulfide. When the data in Table VII are corrected for this hydrolysis they show the entire absence of hydrogen sulfide. In this case, then, only water is produced and the course of the esterification may be satisfactorily represented by equation B.

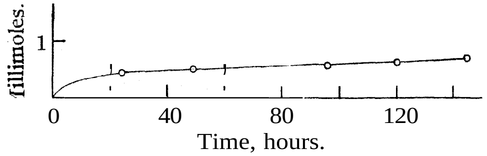


Fig 4.—Triphenylcarbinol, 100°: ———, esterification; - - -, H_2S production

TABLE VII

ESTERIFICATION DATA

Triphenylcarbinol, 0.50 N; thiolacetic acid, 0.506 N; temperature, 100°C.

Time, hrs.	Esterification Millimoles	%	H_2S Produced Millimoles	Corrected
24	0.44	8.7	0.18	0.01
49	.50	10.0	.22	− .03
96	58	11.6	.35	− .07
120	64	12.7	.42	− .10

As a control, bulbs containing only thiolacetic acid and benzene were subjected to prolonged heating. At 76° little or no hydrogen sulfide was observed, but at 100° the quantity became appreciable. From the data in Table VIII, however, it seems that the reaction soon reaches completion, for after ninety-six hours there is neither production of hydrogen sulfide nor disappearance of acid. To determine whether the presence of small amounts of water were responsible for the production of the hydrogen sulfide, a blank was run with thiolacetic acid and benzene 1 N in water, Table IX. Hydrogen sulfide was evolved in larger quantities and the acid disappeared more rapidly. If a decomposition of the acid were taking place we should expect that for a mole of hydrogen sulfide produced at least a mole of acid would disappear. If on the other hand the reaction were purely hydrolytic the total acid concentration would remain constant, since for every mole of thiolacetic acid hydrolyzed a mole of acetic acid would be formed. It is interesting to note in Tables VIII and IX the hydrogen sulfide cannot be quantitatively accounted for by the decrease in the acid concentration. That water is playing an important part, however, is shown by the fact that the acid disappears more rapidly in Table IX than in Table VIII, It is quite possible that both a thermal decomposition and hydrolysis are taking place, but for the purpose of correcting the data in Table VII it is sufficient to know the magnitude of the combined effect.

TABLE VIII

ESTERIFICATION DATA

Blank, 100°C.; thiolacetic acid, 0.966 N

Time, hrs.	Acid decrease, Millimoles	H_2S produced, Millimoles
25	0.04	0.17
48	(.45)	.25
72	.15	.33
96	.24	.43
120	.24	.43

TABLE IX

EXPERIMENTAL DATA

Water, 1.00 N; thiolacetic acid, 0.966 N; temperature, 76°C.

Time, hrs.	Acid decrease, Millimoles	H_2S produced, Millimoles
24	0.11	0.34
48	.16	0.70
72	.28	1.02

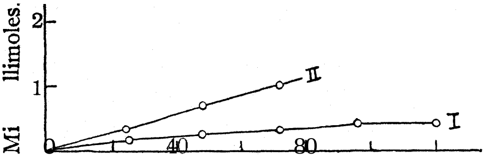
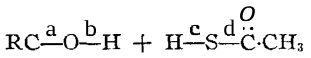


Fig. 5.—H_2S production: I, blank 100°; II, hydrolysis of thiolacetic acid by water.

Theoretical

It seems that the reaction between various alcohols and thiolacetic acid is by no means simple. From the percentage esterification given in Tables IV, V and VI methyl alcohol appears to esterify somewhat more rapidly than ethyl, but both are much more reactive than isopropyl alcohol. The data for triphenylcarbinol, Table VII, are at 100° so that no quantitative comparison can be made, but since the higher temperature was necessary to obtain accurate results, it is unquestionably less reactive than isopropyl alcohol. This is in good agreement with the data given by Petrenko-Kritchenko for these alcohols with acetic acid in Table II. The quantities of hydrogen sulfide evolved by these three reactions show, however, that we are dealing with three distinct processes. Triphenylcarbinol, although the most unreactive, yields only water, which means that only its hydroxyl group enters into the reaction. Methyl and ethyl alcohols while much more reactive can split off either hydroxyl or hydrogen. Isopropyl alcohol is but moderately reactive, yet only its hydrogen takes part in the reaction.

In dealing with esterification processes it is not sufficient to know the relative strengths of the bindings of the —OH and —H in the alcohols only, but one must also consider these bonds in the acids with which they react. For example, in the reaction



$$RC\overset{a}{\text{—}}O\overset{b}{\text{—}}H + H\overset{c}{\text{—}}S\overset{d}{\text{—}}\overset{O}{\overset{\cdot\cdot}{C}}\cdot CH_3$$

when R is $(C_6H_5)_3C$— the bonds a and c split much more easily than the bonds b and d; therefore water is the only product obtained. When R is $(CH_3)_2CH$— bonds b and d are much more easily broken than a and c; therefore only hydrogen sulfide is obtained. When, however, R is CH_3— or C_2H_5— the total energy necessary to break the bonds a and c cannot be very different from that required to break b and d, so that in this case both water and hydrogen sulfide are obtained. From the relative amounts of the two, however, it seems that b and d are the more easily split. Other alcohols will undoubtedly show great differences in the ease with which these two pairs of bonds are split and consequently yield varying proportions of water and hydrogen sulfide.

Since the rate and also the products formed depend not only upon the relative strength of binding in the alcohol but in the acid as well, the same alcohols may not react in the same manner with different acids. In the case of hydrogen chloride the —OH must be furnished by the alcohol so that the constants in Table II are probably a good indication of the relative strengths of binding of this group in the six alcohols studied. This is not the case, however, with trichloroacetic acid, whose —OH is probably more firmly bound than that in acetic acid. If we further assume that the —H is more labile in trichloroacetic than in acetic acid, then one can understand why the constants for the tertiary alcohols are higher than those for their secondary homologs when trichloroacetic acid is used but lower with acetic acid. Trichlorothiolacetic acid should yield water or hydrogen sulfide or both depending upon the structure of the alcohol, but undoubtedly in proportions quite different from thiolacetic acid. These should be interesting in comparison with the data in Table II and it is our hope to consider them in a later communication.

Summary

The products of the reaction of thiolacetic acid with a number of alcohols have been studied quantitatively. Isopropyl alcohol yields only hydrogen sulfide and the normal ester; triphenylcarbinol only water and the thiol ester; methyl and ethyl alcohol give about 78% hydrogen sulfide and 22% water. The question of the mechanism of esterification in general is considered and an explanation of certain anomalies is attempted.

PRINCETON, NEW JERSEY

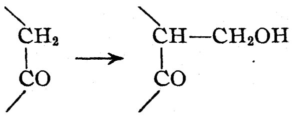
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

CONDENSATIONS BETWEEN FORMALDEHYDE AND MONOKETONES. I. CONDENSATION OF 5-ACETYL-8-HYDROXYQUINOLINE WITH ALDEHYDES

BY KONOMU MATSUMURA AND CHUSABURO SONE

RECEIVED DECEMBER 16, 1930 PUBLISHED APRIL 6, 1931

Many researches relating to the condensation between a methyl or methylene group adjacent to a ketone and aromatic or cyclic aldehyde have been published, whereas, as far as the authors are aware, except in the case of the pyrazolone series, there are only a few previous records of condensation with formaldehyde. K. Goto and his co-workers,[1] in the course of investigations of sinomenine, an alkaloid from *sinomenium acutum*, have found that on refluxing sinomenine, which contains a methylene group adjacent to a carbonyl in its molecule, with an excess of formaldehyde a condensation between them results in the formation of an hydroxymethyl compound in accordance with the scheme



In the present investigation, on treating 5-acetyl-8-hydroxyquinoline with formaldehyde (40%) in a manner similar to that used for sinomenine, it is found that a condensation has taken place between them, but contrary to expectation, resulting in the formation of ω-methylene-bis-5-acetyl-8-hydroxyquinoline (I).

Furthermore, the reaction of 5-acetyl-8-benzoyloxyquinoline and formaline gives ω-methylene-bis-5-acetyl-8-benzoyloxyquinoline. It is evident in view of the latter fact that the presence of a free hydroxyl

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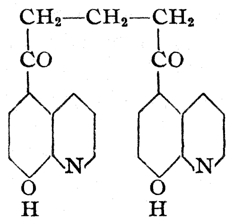
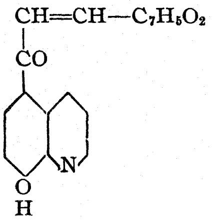
[1] Goto, Shishido and Inaba, *Bull. Chem. Soc., Japan*, 5, 315 (1930).



I



II

group in the molecule would not have any necessary part in the condensation. On the other hand, on treating acetophenone with formaldehyde in the same way or even in the presence of pyridine, acetophenone can be recovered without any notable loss (the, identification is confirmed by the melting point and mixed melting point test of its oxime (m. p. 160–161.5°)). This last failure makes it seem likely that the presence of an amino group in the molecule may serve to facilitate the condensation in any way. A search of the literature reveals that the reaction of salicylaldehyde with acetophenone[2] gives chiefly salicylidene-diacetophenone, while under similar conditions, with **indanone,**[3] it gives salicylidene-indanone. The reaction of 5-acetyl-8-hydroxyquinoline and piperonal, in the **present** work, is found to afford w-piperonylidene-5-acetyl-8-hydroxyquinoline (II), following the course of the latter kind of condensation.

Experimental

α-Methylene-bis-5-acetyl-8-hydroxyquinoline.—A mixture of 0.5 g. of 5-acetyl-8-hydroxyquinoline and 2.5 cc. of formaldehyde (40%), which contains an appreciable amount of a precipitate of paraformaldehyde, is refluxed for two hours. The resulting white precipitate is filtered, on cooling, and washed; yield, 0.5 g. It is recrystallized from nitrobenzene into colorless columns, m. p. >315°. It is sparingly soluble in boiling benzene and alcohol. Its alcoholic solution gives a green coloration with ferric chloride.

Anal. Subs., 5.325 mg.: CO_2, 13.942; H_2O, 2.014. Subs., 4.200: CO_2, 11.019; H_2O, 1.893. Subs., 5.554: N_2, 0.368 cc. (28°, 753.5 mm.). Calcd. for $C_{23}H_{18}O_4N_2$: C 71.50; H, 4.66; N, 7.25. Found: C, 71.41, 71.55; H, 4.20, 5.01; N, 7.17.

The hydrochloride gives yellow needles from hydrochloric acid (10%). It is insoluble in water and does not melt at 300°, decolorizing at 170–220".

Anal. (Water of crystallization). Subs., 0.0830: H_2O, 0.0168. Calcd. for $C_{23}H_{18}O_4N_2 \cdot HCl \cdot 6\ H_2O$: H_2O, 20.36. Found: H_2O, 20.24. Subs., 4.640: AgCl, 1.553. Calcd. for $C_{23}H_{18}O_4N_2 \cdot HCl$: Cf, 8.40. Found: Cl, 8.28.

The **monoxime** gives colorless prisms from nitrobenzene, m. p. 295–300° (decomp.).

Anal. Subs., 3.777: N_2, 0.327 cc. (13.5°, 768 mm.). Calcd. for $C_{23}H_{19}O_4N_3$: N, 10.47. Found: N, 10.29.

ω-Methylene-bis-5-acetyl-8-acetoxyquinoline.—A mixture of 0.2 g. of ω-methylene-bis-5-acetyl-8-hydroxyquinoline, 8 g. of acetic anhydride and 0.5 g. of sodium acetate is

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[2] Cornelson and Kostanecki, *Ber.*, 29, 242 (1896).

[3] Feuerstein, *ibid.*, 34, 413 (1901).

warmed for two and one-half hours on the water-bath. On pouring into crushed ice, after being cooled, the reaction product separates as oily drops which soon turn to a colorless solid (0.2 g.). It crystallized from ethyl acetate into colorless prisms, m. p. 234–235°. It is easily soluble in chloroform, hot alcohol (with a partial hydrolysis). and moderately in hot benzene, but sparingly in ether.

Anal. Subs., 4.783: CO_2, 12.130; H_2O, 2.075. Subs., 3.842: N_2, 0.218 cc. (31°, 760 mm.). Calcd. for $C_{27}H_{22}O_6N_2$: C. 68.94; H, 4.68; N, 5.96. Found: C, 69.16; H, 4.82; N, 6.10.

5-Acetyl-8-benzoyloxyquinoline gives colorless columns from hot alcohol, m. p. 168°. It is easily soluble in benzene and chloroform but sparingly in ether.

Anal. Subs., 5.037: N_2, 0.212 cc. (15°, 767.5 mm.). Calcd. for $C_{18}H_{13}O_3N$: N, 4.81. Found: N, 4.95.

ω-Methylene-bis-5-acetyl-8-benzoyloxyquinoline.—A mixture of 0.6 g. of 5-acetyl-8-benzoyloxyquinoline. 7 cc. of formaldehyde and some alcohol is refluxed for fourteen hours. On cooling, the separated solid (0.3 g.) is filtered and recrystallized from nitrobenzene. It gives colorless prisms, m. p. >315°.

Anal. Subs., 6.738: N_2, 0.282 cc. (15°, 772 mm.). Calcd. for $C_{37}H_{26}O_8N_2$: N, 4.71. Found: N, 4.95.

ω-Piperonylidene-5-acetyl-8-hydroxyquinoline.—A solution of 0.4 g. of sodium hydroxide in the same quantity of water is added to the warm solution of 0.19 g. of 5-acetyl-8-hydroxyquinoline and 0.15 g. of piperonal in 2 g. of alcohol with stirring. The resulting yellow paste, after standing for twenty-four hours with some water added, is acidified with dilute hydrochloric acid, and then an excess of sodium acetate is added. The resulting yellow precipitate is filtered and washed; yield, 0.3 g. It crystallizes from alcohol into yellow needles, m. p. 178–179°.

It is soluble in alcohol, benzene and ether, but insoluble in dilute mineral acid and alkali. The alcoholic solution gives a green color reaction with ferric chloride and the solution in concd. sulfuric acid assumes a purple-red color but decolorizes on addition of water.

Anal. Subs., 3.284: CO_2, 8.600; H_2O, 1.291. Subs., 5.475, 6.115: N_2, 0.214 cc. (30.5°, 762 mm.), 0.233 cc. (25.5°, 760 mm.). Calcd. for $C_{19}H_{13}O_4N$: C, 71.47; H, 4.08; N, 4.39. Found: C, 71.42; H, 4.37; N, 4.07, 4.21.

The writers, hereby, desire to express their hearty thanks to Professor Hata for the interest which he has kindly taken in this work and to Professor Kakuji Goto for the suggestion at which this work was done.

Summary

1. Condensation of 5-acetyl-8-hydroxyquinoline with formaldehyde gives ω-methylene-bis-5-acetyl-8-hydroxyquinoline.

2. Condensation of 5-acetyl-8-hydroxyquinoline with piperonal gives w-piperonylidene-5-acetyl S-hydroxyquinoline.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

THE BECKMANN REARRANGEMENT WITH QUINOLINE COMPOUNDS

BY KONOMU MATSUMURA AND CHUSABURO SONE

RECEIVED DECEMBER 16, 1930 PUBLISHED APRIL 6, 1931

Schroeter, in an earlier research, found that the Beckmann rearrangement with pivalophenone oxime may be able to proceed in two opposite directions in accordance with the type of reagent used.[1] This paper represents a similar instance in the quinoline series. In the previous paper[2] it was definitely established that 5-acetyl- and 5-benzoyl-8-hydroxyquinoline oximes in the Beckmann rearrangement with hydrogen chloride, glacial acetic acid and acetic anhydride, give 5-acetamino- and 5-benzoylamino-8-hydroxyquinoline (I and II), respectively.

$$\underset{\text{I}}{CH_3CONHC_9H_6ON} \qquad \underset{\text{II}}{C_6H_5CONHC_9H_6ON} \qquad \underset{\text{III}}{C_6H_5NHCOC_9H_6ON}$$

In a subsequent investigation it was found that 5-benzoyl-8-hydroxyquinoline oxime, on treatment with thionyl chloride, gave an anilide of 8-hydroxyquinoline-5-carboxylic acid (111), and on hydrolysis with hydrochloric acid, the latter gave 8-hydroxyquinoline-5-carboxylic acid [m. p. 273° tdec.)]. On treating 8-hydroxyquinoline with carbon tetrachloride and potassium hydroxide in alcohol solution, Lippmann and Fleissner obtained an 8-hydroxyquinoline-carboxylic acid [m. p. 280° (dec.)] which gave quinolinic acid on oxidation with potassium permanganate and dibromo-8-hydroxyquinoline (m. p. 193°) on bromination.[3] The experimental data given by these authors make it seem likely that the compound which they obtained would be 8-hydroxyquinoline-5-carboxylic acid, identical with what we have now obtained, but some inconformities in their properties are noticed between them (on pouring in water, the hydrochloride of the authors' compound separates free base, while that of Lippmann and Fleissner is stated to be easily soluble). In order to clear up this matter, the experimental work of Lippmann and Fleissner was repeated and the identity was definitely established. To return to the oxime rearrangement, 5-benzoyl-8-hydroxyquinoline oxime, on treatment with concd. sulfuric acid, is found to give a sulfonated 8-hydroxyquinoline-5-carboxylic acid anilide, and on hydrolysis with hydrochloric acid (20%), the latter gives 8-hydroxyquinoline-5-carboxylie acid. Concerning the position of the sulfonic acid group, no definite proof can be obtained, but the sulfonated compound gives a red color reaction with diazotized sulfanilic acid in alkaline solution. This seems to indicate that the position ortho to the hydroxyl group is not occupied.

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[1] Schroeter, *Ber.*, 44, 1201 (1911).

[2] Matsumura, THIS JOURNAL, 52, 4433 (1930).

[3] Lippmann and Fleissner, Ber., 19, 2467 (1886); *Monatsb.*, 8, 311 (1887).

Moreover, 5-acetyl-8-hydroxyquinoline oxime, in a similar treatment, does not give rise to sulfonation. These facts seem to favor the opinion that the sulfonic acid group might perhaps be in the aniline molecule and then probably in the para position to the amino group.

5-Acetyl-8-hydroxyquinoline oxime, on the other hand, on treating either with thionyl chloride or with sulfuric acid, gives, in either case, 5-acetamino-8-hydroxyquinoline, the same product that is obtainable on treatment with hydrogen chloride, glacial acetic acid and acetic anhydride.

Experimental

8-Hydroxyquinoline-5-carboxylic Acid Anilide.—Thionyl chloride (10 cc.) is added to the cooled solution (0°) of 5-benzoyl-8-hydroxyquinolineoxime (1 g.) in dry ether (150 cc.) with stirring. The resulting yellow precipitate is filtered, after standing for three hours at room temperature (25°), and washed with ether.

On dissolving the precipitate in cold water and making alkaline with sodium carbonate, colorless crystals separated; yield, 1 g. It gives yellowish-white thin plates with a silky luster from alcohol, m. p. 211–212°. It is easily soluble in alcohol, fairly soluble in hot benzene and chloroform, sparingly in ether and insoluble in water.

In this reaction, on using chloroform instead of ether as solvent, the same reaction product can be obtained in a far inferior yield.

Anal. Subs., 4.145 *mg.*: N_2, 0.376 cc. (23°, 769 mm.). Calcd. for $C_{16}H_{12}O_2N_2$: N, 10.60. Found: N, 10.28.

The sulfate gives yellow needles from alcohol, decomposing at 211–215°. When water is poured in, it separates as the free base.

Hydrolysis of **8-Hydroxyquinoline-5-carboxylic Acid Anilide.**—Two tenths gram of 8-hydroxyquinoline-5-carboxylic acid anilide and 8 g. of hydrochloric acid (20%) were refluxed for six hours. On cooling, the resulting crystals of the hydrochloride of 8-hydroxyquinoline-5-carboxylicacid were filtered. The filtrate, on being made alkaline, gave an odor specific to aniline, and a deep violet coloration when in contact with a solution of bleaching powder. The hydrochloride was dissolved in dilute ammonia and on acidification with acetic acid, yellow needles of 8-hydroxyquinoline-5-carboxylic acid separated; yield, 0.1 g. It crystallizes from alcohol to egg-yellow, stout needles, melting at 273° (uncorr.) with decomposition, after preliminary subliming in a sealed capillary. It is moderately soluble in hot alcohol and hot acetone, but difficultly so in ether, chloroform and benzene, and easily soluble in dilute mineral acid and alkali. The alcoholic solution gives a green color reaction with ferric chloride. An attempt to prepare the chloroplatinate was unsuccessful.

Anal. Subs., 4.977: CO_2, 11.608; H_2O, 1.770. Subs., 3.603: N_2, 0.245 cc. (29°, 760.5 mm.). Calcd. for $C_{10}H_7O_3N$: C, 63.49; H, 3.70; N, 7.40. Found: C, 63.61; H, 3.95; N, 7.35.

The **hydrochloride** gives colorless columns from hydrochloric acid (10%), m. p. 239° (decomp.), and separates free base on pouring in water.

Anal. Subs., 5.000: AgCl, 3.149. Calcd. for $C_{10}H_7O_3N{\cdot}HCl$: Cl, 15.74. Found: Cl, 15.58.

The neutral barium salt gives yellow needles from hot water. It is fairly soluble in water but insoluble in alcohol.

Anal. (water of crystallization) Subs., 0.0315: H_2O, 0.0061. Calcd. for $(C_{10}H_6O_3N)_2Ba{\cdot}5.5H_2O$: H_2O, 16.18. Found: H_2O, 16.19. Subs., 5.889: $BaSO_4$, 2.651. Calcd. for $(C_{10}H_6O_3N)_2Ba$: Ba. 26.75. Found: Ba, 26.51.

8-Acetoxyquinoline-5-carboxylic acid gives light yellow prisms from ethyl acetate, decomposing at 312°.

Anal. Subs., 5.101: CO_2, 11.638; H_2O, 1.838. Subs., 5.215: N_2, 0.281 cc. (20°, 754.5 mm.). Calcd. for $C_{12}H_9O_4N$: C, 62.33; H, 3.90; N, 6.05. Found: C, 62.22; H, 4.00; N, 6.09.

8-Methoxyquinoline-5-carboxylic Acid.—A methyl alcohol suspension of 8-hydroxyquinoline-5-carboxylic acid was treated with ethereal diazomethane and the resulting difficultly crystallizable dimethyl derivative was hydrolyzed with alcoholic potassium hydroxide solution. The final product was recrystallized from alcohol into small yellow crystals, m. p. 225–226° (dec.).

Anal. Subs., 3.634: AgI, 4.116 Calcd. for $C_{11}H_9O_3N$: OCH_3, 15.27. Found: OCH_3, 14.95.

Sulfonated **8-Hydroxyquinoline-5-carboxylic** Acid **Anilide.**—A solution of 5-benzoyl-8-hydroxyquinoline oxime (0.5 *g.)* in concd. sulfuric acid *(5* g.) was kept at 100° for an hour. On pouring onto crushed ice (20 g.), a resinous precipitate, which soon turned to a yellow crystalline mass, was formed. It was dissolved in dilute sodium carbonate, reprecipitated with dilute sulfuric acid, and repeatedly washed with cold water; yield, 0.4 g.; m. p. >300°.

It forms in yellowish-white thin plates, practically insoluble in the usual organic solvents, but easily soluble in dilute alkali, and moderately so in boiling water. It gives a green color reaction with ferric chloride, and a red color reaction with diazotized sulfanilic acid and alkali. On hydrolysis with hydrochloric acid (20%), this compound gives 8-hydroxyquinoline-5-carboxylic acid [m. p. 273° (dec.)] in a good yield. An attempt to isolate another component, perhaps sulfanilic acid, failed.

The reaction fluid, however, on being made alkaline, gave no odor of aniline, and after treatment with nitrous acid gives a red coloration with alkaline β-naphthol.

Anal. Subs., 4.545: N_2, 0.339 cc. (28°, 760 mm.). Subs., 5.939: $BaSO_4$, 3.754. Calcd. for $C_{16}H_{11}O_5N_2S$: N, 8.16; S, 9.35. Found: N, 8.15; S, 8.68.

The Reaction of **8-Hydroxyquinoline** and Carbon Tetrachloride.—The compound prepared from 8-hydroxyquinoline (20 g) and carbon tetrachloride by following the method of Lippmann and Fleissner[3] for 8-hydroxyquinoline-carboxylic acid, gives yellow needles from alcohol, melting at 273° (dec.) alone or mixed with 8-hydroxyquinoline-5-carboxylic acid; yield, 3 35 g. The hydrochloride [m. p. 239" (dec.)] separates free base on pouring into water and its methyl ether and acetoxyl derivatives melt at 223–224" (dec.) and 310° (dec.), respectively.

The Beckmann rearrangement of 5-acetyl-8-hydroxyquinoline oxime either with thionyl chloride in chloroform solution or with concd. sulfuric acid gives 5-acetamino-8-hydroxyquinoline (m. p. 217–218°), identified by the mixed melting point test with an authentic specimen.

The writers, hereby, wish to express their hearty thanks to Professor Hata for the interest which he has kindly taken in this work.

Summary

1. 5-Benzoyl-8-hydroxyquinoline oxime, on treatment with thionyl chloride, gives 8-hydtoxyquinoline-5-carboxylic acid anilide and with concd. sulfuric acid gives sulfonated 8-hydroxyquinoline-5-carboxylic acid anilide. Both reaction products, on hydrolysis with hydrochloric acid, give 8-hydroxyquinoline-5-carboxylic acid.

2. 5-Acetyl-8-hydroxyquinolineoxime on treatment either with thionyl chloride or with concd. sulfuric acid gives 5-acetamino-8-hydroxyquinoline.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, MARBURG A L., GERMANY]

THE TITRIMETRIC AND SPECTROMETRIC ANALYSIS OF KETO-ENOL MIXTURES. ALPHA-PHENYLACETOACETIC ESTER

BY KARL V. AUWERS

RECEIVED JANUARY 2, 1931 PUBLISHED APRIL 6, 1931

In a recent paper[1] on the keto-enol equilibrium in a-phenylacetoacetic ester, Post and Michalek have attempted to determine the percentage of the enolic modification, both titrimetrically and spectrometrically. Indirect titration with bromine, by the Kurt Meyer method, gave them an average value of 28.6% of enol, whereas, from its molecular refraction, they calculate the impossible value of 137.13%, which they attribute to the "anomalous" structure of the phenyl group.

These authors also mention, incidentally, that from its molecular refraction the enol content of the unsubstituted acetoacetic ester is 59.2%, whereas, according to the bromine titrations, it contains only 7.7%.

These statements make it appear that spectrochemistry would lead to entirely false results with substances of this type and would not be useful for the analysis of keto-enol mixtures.

However, these authors have overlooked the fact that this problem of the apparent contradiction between the results of the bromine titrations and those of spectrochemistry has long since been investigated and explained.[2]

It has been found that both methods in reality give results which are in sufficient agreement, if certain well-known spectrochemical regularities are correctly taken into account.

Post and Michalek[3] arrive at their values for the enol content by comparing the experimental molecular refraction with the values which they calculate, theoretically, on the basis of atomic refractions. By this procedure, however, correct values are obtained only for the keto forms; those for the enol forms are too low. The molecules of the enolic acetoacetic ester contain a conjugated system of double bonds, the exaltation of which is increased by the hydroxyl group attached to it,[4] since the partial valences

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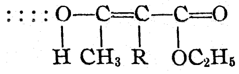
[1] Post and Michalek, THIS JOURNAL, 52, 4358 (1930).

[2] K. v. Auwers, Ann., 415, 169 (1918); K. v. Auwers and H. Jacobsen, *ibid.*, 426, 161 (1921).

[3] Post and Michalek state erroneously that their values have been calculated with the old Brühl refraction equivalents, whereas they have actually used the new Eisenlohr values. It may be mentioned, incidentally, that the accompanying reference number 9, as well as numbers 5 and 7 are not apropos.

[4] K. v. Auwers, Ber., 44, 3514 (1911).

of the oxygen atom, together with the double bond, form a sort of "cumulative" conjugation, as can be seen from the formula



$$::::\underset{H}{O}-\underset{CH_3}{C}=\underset{R}{C}-\underset{OC_2H_5}{C}=O$$

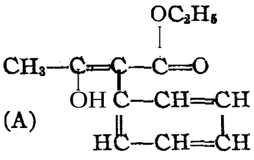
It has been previously shown[6] that by considering all the factors that should be taken into account, the molecular refraction for 100% enolic acetoacetic ester is calculated to be 34.42 instead of 32.62, and this value coincides exactly with the results of Knorr's observations. Furthermore, it has been shown that, according to its molecular refraction, the enol content of the equilibrium ester is 8%, which is in excellent agreement with the titrimetrically determined value. Therefore there is no contradiction, in this case, between the two methods.

α-Phenylacetoacetic Ester.—Post and Michalek calculate the enol content of this compound, refractometrically, from the following figures.

100% Ketone (calcd.)	Found	100% Enol
55.66	57.10	56.71[6]

The third of these figures is, for the reasons previously given, too low. The correct value for the molecular refraction can be approximated with a sort of accuracy by taking into account the following facts.

The specific exaltation of β-hydroxycrotonic ester, *i.* e., the pure enol of acetoacetic ester, has been found to be +1.38. However, substituents introduced into a conjugated system exert an influence on its spectrochemical behavior. The α-phenylacetoacetic ester molecule contains a "crossed conjugation, as shown by the structural formula (A).



(A)

The optical activity of a crossed conjugation, compared to that of a simple conjugation, varies both according to the nature of the parent system and the kind of "disturbing" substituent. In the case under consideration it can be concluded from analogies, which will not be discussed here, that the specific exaltation of the phenylated acetoacetic ester will be approximately as great as that of the parent substance, or at least will not be greater, and probably will be somewhat smaller. Assuming the two to be equal, the molecular exaltation of the pure enol of phenylacetoacetic ester is +2.84, *i. e.*, the molecular refraction of this substance is not 56.71 but 59.56. Then it follows from Post and Michalek's experimental value that the equilibrium ester contains 36.6% enol and not 137.13%.

This value is about 10% higher than those determined titrimetrically by other authors, for their observations yield an average of 26.8%.[7]

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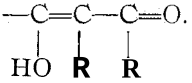
[5] K. v. Auwers, Ref. 4, p. 3530.

[6] The actual values are 55.68 and 56.72.

[7] Post and Michalek calculate, from their investigations, the somewhat higher value of 28.6%.

The difference might mean that the specific exaltation of the phenyl derivative is not equal to that of the parent substance, as assumed; but then it would follow, from the amount of enol which the authors found titrimetrically, that the specific exaltation of the enol of phenylacetoacetic ester, is higher than that of the enol of acetoacetic ester, and therefore that the exalting effect of the crossed conjugated systems is greater than that of simple conjugations. This is, however, in the light of previous spectrochemical experience, unlikely.

Therefore it is necessary to consider the possibility that the indirect bromine titration of α-phenylacetoacetic ester results in too low values, for this has already been established with certainty for various sorts of substances containing the atomic arrangement[8]



$$\underset{\text{HO}}{\overset{|}{—\text{C}}}=\underset{\text{R}}{\overset{|}{\text{C}}}—\underset{\text{R}}{\overset{|}{\text{C}}}=\text{O}.$$

In order to clear this up, I have repeated, in collaboration with Dr. E. Wolter, to whom I extend my sincere thanks for his valuable assistance, the spectrometric and titrimetric investigation of a-phenylacetoacetic ester.

We used both a collection preparation, which was redistilled, and a preparation that was freshly made according to Dimroth and Feuchter's modified directions[9] of Beckh's method.[10] Both preparations had the same properties; they boiled at 141° under a pressure of 9 mm.

SPECTROCHEMICAL CONSTANTS

$d_4^{16.5}$ 1.08915; d_4^{20} 1.086; $n_\alpha^{16.5}$ 1.51065; $n_{\text{He}}^{16.5}$ 1.51513; $n_\beta^{16.5}$ 1.52630; $n_\gamma^{16.5}$ 1.53610; n_{He}^{20} 1.5136

Calculated for....................	M_α	M_D	$M_\beta - M_\alpha$	$M_\gamma - M_\alpha$
$C_{12}H_{14}O{<}O_2''\overline{|3}$ (206.11)	55.32	55.68	1.16	1.86
Found	56.66	67.08	1.45	2.36
M. E.	+1.34	+1.40	+0.29	+0.50
Sp. E.	+0.65	+0.68	+25%	+27%

These data agree satisfactorily with the observations of Post and Michalek; further determinations were therefore considered unnecessary.

Bromine Titrations.—The following titrations, for which samples from both preparations were used, were carried out by the indirect method of Kurt Meyer, in Jena glass vessels. The first two trials were heated for twenty minutes after the addition of potassium iodide, numbers III and IV for thirty minutes and numbers V and VI, one hour.

	Substance, g.	$N/10$ $Na_2S_2O_3$,[a] cc.	Enol, %
I	0.4379	16.4	38.6
II	.3458	12.8	38.1
III	.3732	14.3	39.5

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[8] K. v. Auwers and H. Jacobsen, Ref. 2, p. 165.

[9] Dimroth and Feuchter, *ibid.*, 36, 2243 (1903).

[10] Beckh, *Ber.*, 31, 3160 (1898).

	Substance, g.	$N/10$ $Na_2S_2O_3$,[a] cc.	Enol. %
IV	0.4379	16.5	38.8
V	4385	17.3	40.7
VI	.3579	13.9	40.0

[a] These volumes were calculated by means of the factors of the solutions actually used.

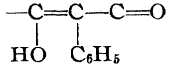
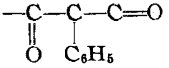
It is apparent that the length of heating has no material effect on the result. This means that conversion was, in every case, complete, and therefore that the indirect procedure is applicable to this substance.

In order to be absolutely certain, the enol content was determined directly, in a final experiment, and verified by indirect titration.

VII *Subs.*, 0.2640 *g.*; $N/10$ Br,[a] 10 *cc.* = 39.0% Enol; $N/10$ $Na_2S_2O_3$,[a] 9.9 *cc.* = 38.7% Enol

The average of all the determinations is 39.2% enol, a value which is approximately that deduced from the refractive index.

It is impossible to state why Post and Michalek found a materially lower value, although their preparation had the same physical constants as that which we investigated. The supposition that in their investigation of the ester it had become more ketonic in alcoholic solution can hardly be correct, for we found the higher values of the enol content, also, when the solutions had stood for several hours or had come to room temperature.

The noteworthy fact that a-phenylacetoacetic ester enolizes to a much greater extent than a-alkyl acetoacetic esters[11] can be explained, following Post and Michalek, by the ionizing influence which the phenyl group exerts on the a-hydrogen atom. It may, however, also be due to the fact that there is present in the enol of that compound the atomic arrangement (C_6H_5—C=C—) which is actually characteristic of styrols. It is known that A^2-styrols, C_6H_5—C—C=C—, have a tendency to pass over into the A^1-isomers, whereas a shift of the double bond in the opposite direction does not take place. In contrast to this, in the olefinic acid a mutual interconversion of Δ^1 and A^2 is possible. Therefore the system  $-\underset{HO}{\underset{|}{C}}=\underset{C_6H_5}{\underset{|}{C}}-C=O$ will show a stronger resistance to conversion into  $-\underset{O}{\underset{\|}{C}}-\underset{C_6H_5}{\underset{|}{C}}-C=O$ than the enols of acetoacetic ester and its alkyl derivatives, and this must result in an increase in the enol content of the equilibrium ester.

Summary

1. The rule that titrimetric **and** spectrometric determinations of the enol content of tautomeric mixtures gives results in satisfactory agreement holds also for a-phenylacetoacetic ester.

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[11] Dieckmann [*Ber.*, 55, *2476* (1922)] has already pointed out the high "enol constants" of phenyl derivatives.

2. Titrimetrically, the enol content of this substance is found to be 39.2% and spectrometrically 36–37%, therefore materially higher than for a-alkyl acetoacetic esters.

3. For a-phenylacetoacetic ester, in contrast to a-alkylacetoacetic ester, the direct bromine titration is just as applicable as the indirect bromine titration.

CHEMISCHES INSTITUT
MARBURG, GERMANY

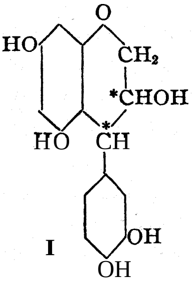
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRISTOL]

STEREOISOMERIC CATECHINS

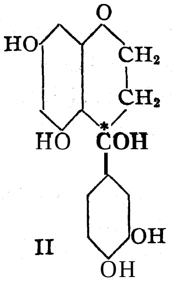
BY R. P. BIGGS, W. L. COOPER, EDITH O. HAZLETON, M. NIERENSTEIN AND PHYLLIS H. PRICE

RECEIVED JANUARY 5, 1931 PUBLISHED APRIL 6, 1931

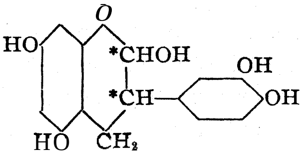
Six stereoisomers are to be expected from acacatechin (I) and three from iso-acacatechin (II), but so far only four have been identified in Nature, namely, *l*- and dl-acacatechin and *l*- and dl-iso-acgcatechin.



I



II



III

The present communication describes two new stereoisomeric catechins, d acacatechin and d-iso-acacatechin. d-Acacatechin accompanied by *dl*-acacatechin was found in mahogany wood from South America and the West Indies and in the Australian Kinos from *Eucalyptus viminalis*, Lab., E. Leucoxylon, Müll. and *Angophora intermedia* D. C., whereas *d*-iso-acacatechin only was identified in the heartwood of *Anarcadium occidentale*, L. Of the other plant materials investigated in the course of the present work, the Malabar Kinos from *Myristica Malabarica*, Larn. and *Pterocorpus Marsupium*, Roxb , and the Australian Kino from *Eucalyptus corymbosa*, Smith, were found to contain 1-acacatechin and dl-acacatechin, whilst Chinese rhubarb, Guarana paste, Kola nuts and the leaves of Uncaria gambir, Roxb. and of *Uncaria acida*, Roxb. all contain *d*-gambir-catechin and dl-gambir-catechin.

The investigation, in view of their red-brown color suggesting the presence of catechin, was also extended to the following plant materials: oak bark,[1] chestnut bark, quebracho wood, hemlock bark, almond skins and cured Virginian and Rhodesian tobacco. None of these materials, however, was found to contain catechin.

The identification of d-iso-acacatechin in Nature completes the iso-acacatechin (II) series, whereas the discovery of d-acacatechin (I) still leaves three more stereoisomeric acacatechins to be accounted for, since they cannot, with any degree of certainty, be identified with d- and *dl*-gambir-catechin.[2]

Whatever the interrelationship between gambir-catechin and acacatechin may prove to be, the chemistry of catechin is faced with the fact that ***eight*** catechins have now been identified in Nature. This, in our opinion, finally disproves the contention that all catechins are stereoisomerides of one and the same parent substance containing ***two*** asymmetric carbon atoms, *as* postulated by Freudenberg's[3] hypothesis, already criticized[4] on other grounds.

On the other hand, if one assumes that gambir-catechin is represented by Formula III, as evident from the work of Drumm, Carolan and Ryan,[5] one realizes that ***fifteen*** catechins are theoretically possible, namely, six stereoisomeric acacatechins (I), three stereoisomeric iso-acacatechins (II) and six stereoisomeric gambir-catechins (III). So far only eight catechins have been identified, which still leaves seven more to be accounted for, and it is proposed to continue the work in this direction. Meanwhile reference is made to a suggestion put forward over a hundred years ago by Nees von Esenbeck,[6] to reserve the name catechin for the substance present in the cutch of *Acacia Catechu* and to refer to the corresponding product present in the cutch of *Nauclea* (syn. *Uncaria*) *gambir* as nauclein. It is perhaps now too late to adopt this suggestion, but there is not the slightest doubt whatever that if catechin and nauclein had been dealt with separately much confusion would have been avoided. In this connection attention must be drawn to the definite line of demarcation between the occurrence of aca- and iso-acacatechin on the one hand and gambir-

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[1] Casparis, *Pharm. Acta Helv.*, 4, 181, 189 (1929), found a catechin-like substance in oak bark. This, however, has not been confirmed by Freudenberg and Oehler, *Ann.*, 483, 140 (1930), who are of the opinion that Casparis had mistaken ellagic acid for catechin.

[2] See Freudenberg and Cohn, *Ber.*, 56, 2127 (1923); Freudenberg, Carrara and Cohn, *Ann.*, 446, 87 (1925); Carrara and Cohn, *Gazz. chim. ital.*, 56, *I*, 134 (1926); Baker, *J. Chem. Soc.*, 1593 (1929); *Drumm,* Carolan and Ryan, *Proc. Royal Irish Acad.. [B]* 39, 114 (1929).

[3] Freudenberg, Bohme and Beckendorff, *Ber.*, 54, 1204 (1921); Freudenberg, Bohme and Purrmann, *ibid.*, 55, 1734 (1922); Freudenberg and Purrmann, *Ann.*, 437, 274 (1924).

[4] Hückel, Neunhöffer, Gercke and Frank, *ibid.*, 477, 159 (1929).

[5] Drumm, Carolan and Ryan, *Proc. Royal Irish Acad.*, [B] 39, 114 (1929).

[6] Nees von Esenbeck, *Büchner's Report*, 33, 171 (1829).

catechin on the other, although it must be noted that Freudenberg and Oehler[7] report the presence of l-acacatechin and d-gambir-catechin in the Kola nut, a point not confirmed by us, since we only found d- and *dl*-gambir-catechin in the material investigated by us, and also in a specimen of Kola nut catechin kindly sent us by Dr. Ultée.

Historical

Some of the materials investigated by us have already been studied by previous workers. Thus mahogany wood was found by Latour and Caseneuve[8] to contain a catechin-like substance, and this was confirmed by Freudenberg, Bohme and Purrmann,[9] who showed it to be dextrorotatory.

Catechin-like substances were also found in the Kinos of Eucalyptus *viminalis* and *Eucalyptus* Leucoxylon by Heckel and Schlagdenhauffen,[10] whereas Maiden[11] and Smith[12] reported the presence of such substances in the Kinos of *Angophora* intermedia and *Pterocorpus Marsupium*, respectively.

The catechin in Chinese rhubarb was investigated by Gilson,[13] who proved it to be d-gambir-catechin. This was confirmed by Freudenberg, Böhme and Purrmann,[9] and now also by us. As regards the presence of catechin in Guarana paste, it must be noted that Kirmsse[14] and Freudenberg and his collaborators[15] have investigated it with no definite success, and similar indefinite results were obtained by Goris[16] and Goris and Fluteaux,[17] and by Casparis[18] in the case of the Kola nut. The results of Freudenberg and Oehler on the catechins present in the Kola nut have already been mentioned.

Experimental

The Kinos, the Guarana paste and the different kinds of wood, in the form of sawdust, were exhaustively extracted with ethyl acetate in a large Soxhlet apparatus. The Kinos and the Guarana paste were finely powdered, passed through a 30-mesh sieve and mixed with ten times their own weight of sand.[19] The ethyl acetate extracts were evaporated to dryness under

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[7] Freudenberg and Oehler, *Ann.*, 483, 140 (1930).

[8] Latour and Caseneuve, *Ber.*, 8, 828 (1875); *Arch. Pharm.*, 208, 558 (1876)

[9] Freudenberg, Bohme and Purrmann, *Ber.*, 55, 1743 (1922).

[10] Heckel and Schlagdenhauffen, *J. pharm. chim.*, [5] 26, 152 (1892)

[11] Maiden, *Pharm* J., [3] 20, 27 (1890).

[12] Smith, *Am* *J. Pharm.*, 68, 676 (1896).

[13] Gilson, *Acad méd. belg.*, [4] 16, 827 (1902).

[14] Kirmsse, *Arch. Pharm.*, 236, 122 (1898).

[15] Freudenberg, Bohme and Purrmann, *Ber.*, 55, 1744 (1922).

[16] Goris, *Compt rend*, 144, 1162 (1907).

[17] Goris and Fluteaux, *Bull. soc. pharmacol.*, *17*, 599 (1910).

[18] Casparis, *Pharm. Acta Helv.*, *4*, 181, 189 (1929).

[19] The sand used was at first treated with dilute hydrochloric acid, then washed with water, alcohol and ether. It was then dried at 100° and powdered.

reduced pressure and the remaining solid powdered and mixed with ten times its own weight of sand. It was then extracted in a Soxhlet apparatus with ether free from alcohol Extraction was continued until no solid was obtained on evaporation of the ether. The solids obtained on evaporation of the ether were dissolved in hot water slightly acidulated with acetic acid,[20] and the solid collected after standing for some time, when as a rule the dl-forms separated first. The catechin fractions thus obtained were recrystallized from water, dried in a vacuum desiccator over concentrated sulfuric acid for several days and acetylated by heating with acetic anhydride. The solid obtained on precipitation with water crystallized from alcohol and a few drops of acetone. The filtrates of the crude catechins were evaporated by standing over concentrated sulfuric acid, the solids thus obtained were then powdered and mixed with sand, again extracted with ether and worked up in the manner described above. The aqueous filtrates were then again solidified and examined in the same way. It was generally found that these third solids contained little or no catechin.

In the case of the leaves of the *Uncaria* species and the Chinese rhubarb, no ethyl acetate extractions were carried out, but the materials were at first exhaustively extracted in a Soxhlet apparatus with chloroform so as to remove chlorophyll, and in the case of Chinese rhubarb chrysophanic acid and such-like substances. The removal of chrysophanic acid from Chinese rhubarb was very tedious, and required continuous extraction for nearly two months. After the extraction with chloroform, the leaves and rhubarb were powdered in a mill and extracted with ether as described. In the case of the Kola nut it was also found necessary to subject the finely broken up material to chloroform extraction before extraction with ether.

In the identification of the different catechins, reliance was laid on the pentaacetyl derivatives, which are remarkable for the ease with which they crystallize and for the sharpness of their melting points. Nearly thirty years' experience with catechin has convinced Nierenstein[21] that very little reliability can be placed on the melting points of the catechins themselves, as these are greatly affected by moisture. This is best illustrated in the case of gambir-catechin,[22] which is reported to melt at 96, 175–177 and 210°, respectively, these variations being due to water of crystallization. In a similar manner, Nierenstein[23] has come to the conclusion that not much confidence can be attached to the melting points of the methoxy derivatives if prepared in the usual way by the action of dimethyl sulfate

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[20] Nierenstein, J. *Chem. Soc., 121,* 609 (1922).

[21] Nierenstein, J. *Indian Chem. Soc.,* 7, 279 (1930).

[22] See Kostanecki and Tambor, *Ber.,* 35,1867 (1902); Clauser, *ibid.,* 36, 101 (1903); Perkin, J. *Chem. Soc.,* 87, 398 (1905).

[23] Nierenstein, THIS JOURNAL, 48, 1964 (1926); 52,4012 (1930).

and alkali, since these derivatives are generally contaminated with by-products, formed through fission of the chromane ring. The following summary gives the melting points and rotations in tetrachloroethane of the pentaacetyl derivatives as used by us as evidence of identity and purity.

	M. p., °C.	$[\alpha]_D$
Pentaacetyl-*l*-acacatechin	151	−12.0°
Pentaacetyl-d-acacatechin	151	+12.0°
Pentaacetyl-dl-acacatechin	160	.....
Pentaacetyl-*l*-iso-acacatechin	171	−29.3"
Pentaacetyl-d-iso-acacatechin	171	+29.3°
Pentaacetyl-dl-iso-acacatechin	193	...
Pentaacetyl-d-gambir-catechin	137	+37.6°
Pentaacetyl-dl-gambir-catechin	156	...

As a check on our melting points of pentaacetyl-dl-acacatechin and pentaacetyl-dl-iso-acacatechin obtained from the naturally occurring *dl*-catechins, these pentaacetates were also prepared by admixture of equal parts of pentaacetyl-*l*-acacatechin with pentaacetyl-d-acacatechin and of pentaacetyl-*l*-iso-acacatechin with pentaacetyl-d-iso-acacatechin. These synthetic pentaacetates proved to be in every respect identical with the pentaacetates of natural origin. Unfortunately, no such check could be carried out on pentaacetyl-dl-gambir-catechin, as only pentaacetyl-*d*-gambir-catechin has so far been identified in Nature.

In the identification of the different pentaacetyl derivatives, we strongly adhered to the constants given above. Where lower melting points or lower rotations were observed, the products were repeatedly recrystallized until these constants were reached. In this we have succeeded in every case. With the single exception of pentaacetyl-d-iso-acacatechin, which has so far only been found in *Anarcadium occidentale*, mixed melting points were taken, and in no case could depressions be observed. All the pentaacetates, dried at 110°, were analyzed in duplicate and were found to agree within the limits of experimental error for $C_{15}H_9O_6(COCH_3)_5$.

We append the following summary showing the quantities of material investigated and the approximate yields of the different catechins obtained.

(1) 56 Kilos mahogany wood from South Africa: 12 g. d-acacatechin and 3.5 g. dl-acacatechin
(2) 42 Kilos mahogany wood from the West Indies: 6 g. d-acacatechin and 6 g. *dl*-acacatechin
(3) 8 Kilos Australian Kino from *Eucalyptus viminalis:* 16 g. d-acacatechin and 22 g. dl-acacatechin
(4) 6 Kilos Australian Kino from *Eucalyptus Leucoxylon:* 5 g. d-acacatechin and 10 g. dl-acacatechin
(5) 9 Kilos Australian Kino from *Angophora intermedia:* 14 g. d-acacatechin and 8 g. dl-acacatechin
(6) 86 Kilos heartwood of *Anarcadium occidentale:* 29 g. d-iso-acacatechin

(7) **4** Kilos Malabar Kino from *Myristica Malabarica:* **3** g. l-acacatechin and **11 g.** dl-acacatechin
(8) **7** Kilos Malabar Kino from *Pterocorpus Marsupium:* **9** g. *l*-acacatechin and **17** g. dl-acacatechin
(9) 6 Kilos Australian Kino from Eucalyptus *corymbosa:* 4 g. *l*-acacatechin and **9** g. dl-acacatechin
(10) **28** Kilos *Uncaria* gambir leaves: **56** g. *d*-gambir-catechin and **6 g.** dl-gambir-catechin
(11) **2.8** Kilos *Uncaria acida* leaves: **9** g. d-gambir-catechin and **4.5** g. *dl*-gambir-catechin
(12) **11** Kilos Chinese rhubarb: **17** g. d-gambir-catechin and **3** g. dl-gambir-catechin
(13) **2** Kilos Guarana paste: **5** g. d-gambir-catechin and 4 g. dl-gambir-catechin
(14) **19** Kilos Kola nuts: **58** g. d-gambir-catechin and 8 g. dl-gambir-catechin

In conclusion, the authors wish to express their thanks to the Colston Research Society of the University for many generous grants, without which this investigation would not have been possible.

Summary

Eight stereoisomeric catechins have been shown to exist in Nature, of which d-acacatechin and d-iso-acacatechin have been discovered in the course of the present investigation.

BRISTOL, ENGLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY].

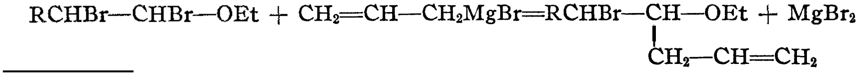
NUCLEAR SYNTHESES IN THE OLEFIN SERIES.
II. 1,4-DIOLEFINS[1]

BY BERNARD H. SHOEMAKER[2] AND CECIL E. BOORD

RECEIVED JANUARY 5, 1931 PUBLISHED APRIL 6, 1931

The nuclear synthesis of unsaturated hydrocarbons previously described[3] has been extended to the synthesis of 1,4-diolefins. This extension has been made possible through the preparation of allylmagnesium bromide by the method described by Gilman and McGlumphy.[4]

The addition of an α,β-dibromoalkyl ethyl ether to a slight excess of allylmagnesium bromide in ether solution leads to the formation of an α-allyl-β-bromoalkyl ethyl ether. It has been found in general that β-bromo



$$\mathrm{RCHBr{-}CHBr{-}OEt + CH_2{=}CH{-}CH_2MgBr = RCHBr{-}\underset{\displaystyle CH_2{-}CH{=}CH_2}{\underset{|}{CH}}{-}OEt + MgBr_2}$$

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[1] Presented before the Organic Division of the American Chemical Society, at Atlanta, Georgia, April, **1930.**

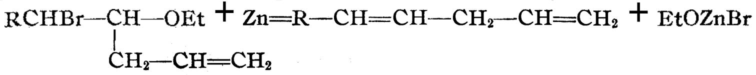
[2] Abstracted from the dissertation presented by Bernard H. Shoemaker in partial fulfilment of the requirements for the Ph.D. degree to the Faculty of the Graduate School of The Ohio State University, June, **1930.**

[3] **Dykstra,** Lewis and Boord, THIS JOURNAL, 52, **3396 (1930).**

[4] Gilman and McGlumphy. Bull. *soc. chim.,* **[4] 43, 1322 (1928).**

ethers are most readily purified by steam distillation. This procedure serves to destroy the residual dibromo ether and yields the desired product in a form which may be further purified by direct distillation under diminished pressure. The p-bromo ethers so purified are obtained as water-white limpid liquids and have been kept for many months without apparent deterioration.

The conversion of the β-bromo ethers into the corresponding unsaturated compounds has also been improved. When the ethyl alcohol, as a medium for the decomposition by zinc, is replaced by n-propyl or n-butyl alcohol, both the speed of the reaction and the yield are greatly increased. The increase in reaction velocity is doubtless due in part to the higher boiling point temperatures of the new solvents but it is also due in part to the greater solubility of ethoxyzinc bromide in the new media, so that the surface of the metal is kept clean.



$$RCHBr{-}\underset{\displaystyle CH_2{-}CH{=}CH_2}{\underset{|}{CH}}{-}OEt + Zn = R{-}CH{=}CH{-}CH_2{-}CH{=}CH_2 + EtOZnBr$$

The observations previously made upon the relation of the boiling points of the a-olefins to the corresponding saturated hydrocarbons has been fully confirmed.[5] The data as relating to diolefins having five, six and seven carbon atoms all in a continuous chain are shown in Table I. It will be observed that those dienes having a double bond at each end of the chain boil lower than the corresponding a-olefins. When one of the double bonds is moved away from the end of the chain, the boiling point is raised. As one of the double bonds is moved stepwise toward the one at the opposite end of the chain, the boiling point continues to rise. If both are moved away from the ends of the chain, the boiling point is still higher. The data for the seven carbon atom chains are not complete but in so far as available they stand in good agreement with the above rules.

It has been observed frequently that the tetrabromo paraffins exist in isomeric forms.[6] The same phenomena exist among the polybromo fatty acids.[7] The tetrabromides of the 1,4-diolefins show this same tendency to isomerism. In the case of 1,4-pentadiene the solid phase is obtained in

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[5] It has come to our attention that Baudenghien, Bull. *soc. chim. Belg.*, *31*, 160 (1922), has used the same principle in discussing the identity of certain butenols. He cites the following cases

$CH_3{-}CHOH{-}CH{=}CH_2$	b. p. 97°	$CH_3{-}CHCl{-}CH_2{-}CH_3$	b. p. 68°
$CH_3{-}CHOH{-}CH_2{-}CH_3$	b. p. 99°	$CH_3{-}CHOAc{-}CH{=}CH_2$	b. p. 111"
$CH_3{-}CHCl{-}CH{=}CH_2$	b. p. 64°	$CH_3{-}CHOAc{-}CH_2{-}CH_3$	b. p. 113°

So far as we are aware the relationship has not been generalized.

[6] Magnanini, *Gazz. chim. ital.*, *16*, 390–392 (1886); Fournier, Bull. *soc. chim.*, *[3]15,403* (1896); Ciamician and Anderlini, *Ber.*, 22, 2498 (1889); Griner, *Ann, chim.*, [6] 26,325 (1892).

[7] Rollett, Z. *physiol. Chem.*, *62*, 410, 421 (1909); Erdmann and Bedford, *Ber.*, 42,1324 (1909); Brown and Beal, THIS JOURNAL, 45,1301 (1923).

almost quantitative yield. As the number of carbon atoms is increased, the percentage of the solid isomer is decreased.

TABLE I

BOILING POINTS OF THE DIOLEFINS

Hydrocarbons	Boiling points, °C	Investigator
$CH_2=CH-CH_2-CH_2-CH_3$	29.5–31	[a] Dykstra, Lewis, Boord
$CH^2=CH-CH_2-CH=CH_2$	28.5–29.2	Present paper
	25.8–26.2	[b] Kogerman
$CH_2=CH-CH=CH-CH_3$	48	[c] Auwers and Westermann
$CH_2=C=CH-CH_2-CH_3$	45	[d] Bouis
$CH_3-CH=C=CH-CH_3$	49–51	[e] Kukuritschkin
$CH_2=CH-CH_2-CH_2-CH_2-CH_3$	63.35	[f] van Risseghem
$CH_2=CH-CH_2-CH_2-CH=CH_2$	59.57	[g] Cortese
$CH_2=CH-CH_2-CH=CH-CH_3$	64.3–64.6	Present paper
$CH_2=CH-CH=CH-CH_2-CH_3$	72–74	[h] Fournier
$CH_2=C=CH-CH_2-CH_2-CH_3$	78	[d] Bouis
$CH_3-CH=CH-CH=CH-CH_3$	77–78, 81.5–82	[i] Prévost
$CH_2=CH-CH_2-CH_2-CH_2-CH_2-CH_3$	94.45	[j] Bourguel
$CH_2=CH-CH_2-CH=CH-CH_2-CH_3$	92–92.3	Present paper
$CH_2=C=CH-CH_2-CH_2-CH_2-CH_3$	105–6	[d] Bouis
$CH_3-CH=CH-CH=CH-CH_2-CH_3$	107	[c] Auwers and Westermann

[a] Dykstra, Lewis and Boord, THIS JOURNAL, 52, 3396 (1930); [b] Kogerman, *ibid.*, 52, 5060 (1930); [c] Auwers and Westermann, *Ber.*, **54B**, 2998 (1921); [d] Bouis, *Ann. chim.*, 9, 440 (1928); [e] Kukuritschkin, J. *Russ. Phys.-Chem. Soc.*, Chem. Pt., 35, 877 (1903); [f] van Risseghem, *Bull. soc. chim. Belg.*, 35, 328 (1926); [g] Cortese, THIS JOURNAL, 51, 2268 (1929); [h] Fournier, *Bull. soc. chim.*, [3] 15, 402 (1896); [i] Prévost, Ann. *chim.*, [10] 10, 142 (1928). P. believes this diene exists in two forms as indicated; Brühl, *Ber.*, **41**, 3713 (1909), gives 77–78'; Reif, *ibid.*, 41, 2744 (1908), gives 80–82°; Bourguel, *Bull. soc. chim.*, **41**, 1475 (1927). Soday, in unpublished work done in this Laboratory, finds 94.3°.

Experimental Part

a-Chloroalkyl Ethyl Ethers, $R-CHCl-O-C_2H_5$.—The method previously described[8] has been improved and extended to the preparation of α-chloropropyl-, and a-chloro-n-butyl ethyl ethers. The darkening of the chloro ether may be avoided if the reaction is conducted so as to avoid undue mixing of the ethereal and aqueous layers. The preparation is best made by placing equimolar quantities of the aldehyde and absolute alcohol in a short-stemmed separatory funnel immersed in a freezing mixture. Hydrogen chloride is then led in in such a manner that it does not pass through the aqueous layer which soon begins to form and violent agitation is avoided. This addition is discontinued when the gain in weight corresponds to a 5% excess over the theoretical value. The aqueous layer is drawn off and the crude chloro ether dried over granular calcium chloride. The excess hydrogen chloride is removed by maintaining the product under diminished pressure, the granules of calcium chloride serving as bumping stones during this process. The product from a well-regulated experiment will be water white. For the purpose of synthesis this crude product is not distilled because of loss by decomposition. The yields of crude chloro ethers are shown in Table II. The physical constants and analyses are for the purified products.

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[8] Swallen and Boord, THIS JOURNAL, 52, 654 (1930).

TABLE II

α-CHLOROALKYL ETHYL ETHERS, $R—CHCl—OC_2H_5$

R	Yield, %	B. p., °C	d_4^{20}	n^{20}	Analyses, Cl, % Calcd.	Found
CH_3	78.7[a]	....	..	....	....	....
C_2H_5	74	34–36 (25 mm.)	0.954	1.4120	28.93	28.59 28.65
n-C_3H_7	81[b]	49–51 (25 mm.)	.938	1.4168	25.96	24.75 24.68

[a] Swallen and Boord, Ref. 8. [b] James Vaughn (unpublished Master's Thesis, The Ohio State University, 1926) obtained this compound in a yield of 37% of purified product, b. p. 55° (40 mm.); chlorine found, 26.03%.

α,β-Dibromoalkyl Ethyl Ethers, $R—CHBr—CHBr—O—C_2H_5$.—In the bromination of the α-chloro ethers it has been found advantageous to avoid aspirating the product with a current of air as previously has been done. A few granules of calcium chloride were added and the reaction mixture maintained under diminished pressure for several hours. The granular calcium chloride serves the dual purpose of drying agent and bumping stones in freeing the product of dissolved hydrogen chloride. The dibromo ethers prepared in this way are pale straw colored liquids. The yields given in Table III are for the crude products. The physical constants and analyses are for products further purified by a single fractionation.

TABLE III

α,β-DIBROMOALKYL ETHYL ETHERS, $R—CHBr—CHBr—O—C_2H_5$

R	Yield, %	B. p., °C.	d_4^{20}	n^{20}	Analyses, Br, % Calcd.	Found
H[a]	92–93	....	...	....	...	....
CH_3	90–97	79–82 (20 mm.)	1.649	1.5000	64.99	64.88
C_2H_5	90	99–101 (27 mm.)	1.564	1.4968	61.49	60.69 61.11

[a] Swallen and Boord, Ref. 8; Dykstra, Lewis and Boord, Table I, Ref. a.

Allylmagnesium Bromide, $CH_2{=}CH—CH_2MgBr$.—Seventy-five grams of magnesium turnings was placed in a three-necked flask and covered with 200 cc. of anhydrous ether. The flask was fitted with a mechanical stirrer and a reflux condenser and submerged in an ice-bath. One gram mole of allyl bromide dissolved in 570 cc. of anhydrous ether was added dropwise over a period of eight to nine hours. The formation of the Grignard reagent was started by crushing one or two pieces of magnesium turnings in a test-tube under an ether solution of allyl bromide and adding this to the main portion. The reaction started immediately.

After the addition of allyl bromide was completed, 500 cc. of the ether solution of the Grignard reagent was decanted and the remaining solution replenished by an additional portion of 30–35 g. of magnesium. One-half gram mole of allyl bromide dissolved in 285 cc. of anhydrous ether was then added at the same rate as before. After the addition had been completed, the reaction mixture was allowed to stand for one-half hour. The ether solution was then decanted, care being taken to avoid carrying over any metallic magnesium. The turnings were washed with anhydrous ether and the washings added to the main portion.

The ether solution of allylmagnesium bromide was made up to a definite volume and titrated for reagent content by the method of Gilman, Wilkinson, Fishel and Meyers.[9] The yield of allylmagnesium bromide varied from 70 to 82% and was higher for the larger runs.

α-Allyl-β-bromoalkyl Ethyl Ethers, $R—CHBr—CH(C_3H_5)—O—C_2H_5$.—The ether

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[9] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, 45, 150 (1923).

solution of allylmagnesium bromide was placed in a two-liter three-necked flask which had been provided with a mechanical stirrer and reflux condenser. The flask was surrounded by a freezing mixture and the appropriate dibromoalkyl ethyl ether dissolved in an equal volume of anhydrous sulfuric ether added slowly to a slight excess of the Grignard reagent. The condensation proceeded very rapidly. After all of the dibromo ether had been added the flask was allowed to stand at room temperature for one or two hours.

The reaction mixture always separated into two layers, the lower one consisting essentially of magnesium bromide etherate. The entire mass was hydrolyzed by pouring into a beaker of cracked ice and acidifying with dilute hydrochloric acid. The ether layer was separated and slowly distilled on a steam-bath until all of the sulfuric ether had been removed. The residual oil was then distilled with steam. The β-bromo ether, which separated at the bottom of the steam distillate, was drawn off, washed with water and dried over calcium chloride and a small amount of solid sodium hydroxide. The α-allyl-β-bromoalkyl ethyl ethers were finally purified by fractional distillation under diminished pressure.

In all cases a low-boiling portion was obtained which became larger in amount as the molecular weight of the β-bromo ether increased. This proved to be due to the decomposition of the main product by loss of hydrogen bromide and was so pronounced in the case of the branching chained product from isobutyraldehyde that pure α-allyl-β-bromoisobutyl ethyl ether could not be isolated.

The yields, physical constants and analyses of the α-allyl-β-bromoalkyl ethyl ethers prepared are shown in Table IV.

TABLE IV

α-ALLYL-β-BROMOALKYL ETHYL ETHERS, $R—CHBr—CH(C_3H_5)—OC_2H_5$

R	Yield, %	B. p., °C.	d_4^{20}	n^{20}	Analyses, Br, % Calcd.	Found	
H	48–50	69–71 (21 mm.)	1.225	1.4592	41.41	41.48	
		84–86 (33 mm.)				41.51	
CH_3	38–43	72–75 (16 mm.)	1.162	1.4592	38.60	36.51	36.71
C_2H_5	37–45	88–92 (18 mm.)	1.150	1.4606	36.16	34.71	34.36

Preparation of 1,4-Diolefins

It has been found advantageous to substitute the higher boiling propyl and butyl alcohols for ethyl alcohol as the solvent medium in the decomposition of the β-bromo ethers with zinc. The yield of 1,4-pentadiene by the action of zinc dust upon α-allyl-β-bromoethyl ethyl ether in n-butyl alcohol is above 65% in four hours, whereas in ethyl alcohol it is not more than 30% at the end of five days.

1,4-Pentadiene, $CH_2═CH—CH_2—CH═CH_2$.—One hundred and eight grams of a-allyl-j3-bromoethyl ethyl ether was dissolved in 125 cc. of n-butyl alcohol in a one-liter three-necked flask. The flask was provided with a mechanical stirrer and a reflux condenser. The water in the condenser was kept between 35–60° so that the solvent medium was largely condensed and returned to the generating flask while the more volatile 1,4-pentadiene (b. p. 30°) passed through the reflux into a second condensing system and was collected in a receiver immersed in an ice-bath. One hundred grams of zinc dust was added portion-wise as the reaction proceeded. The speed of the reaction was so regulated that the pentadiene distilled over at approximately one drop per second as a maximum. In four hours 25 g. or 65.8% of the theoretical yield was obtained. After drying over calcium chloride it was distilled twice from metallic sodium to remove any traces of butyl alcohol. The yield of purified product was 20 g. or 52.6%. The boiling range of the major portion was 28.5–29.2° (742 mm.).[9a]

1,4-Hexadiene, $CH_2{=}CH{-}CH_2{-}CH{=}CH{-}CH_3$.—One hundred ten grams of α-allyl-β-bromopropyl ethyl ether, 225 cc. of n-propyl alcohol and 100 g. of zinc dust were refluxed for fifteen hours. Thirty-eight grams of crude distillate was collected and washed five times with one-half its volume of ice cold water. The product was dried over calcium chloride and distilled twice from metallic sodium to remove absorbed alcohol. The purified product weighed 29.4 g., had a boiling range of 63–64.8° and represented a 67.4% yield. The major portion distilled at 64.3–64.6" under 745 mm. pressure.

This boiling point is in good agreement with 64–66° as given by Griner[10] for a compound prepared by the action of hydriodic acid upon diallyl and subsequent decomposition of the iodide thus obtained by alcoholic potassium hydroxide. Merling[11] has also described a product as 1,4-hexadiene. This product was obtained by heating pentenyltrimethylammonium hydroxide in an oil-bath to 160° or in better yield by heating the same quaternary ammonium hydroxide with water in a sealed tube at 180°. Since the boiling point of his diene (80–83°) was too high for diallyl, which he had expected to obtain, he has offered a reaction mechanism to show isomerization to 1,4-hexadiene. In the light of the present work and that of Griner it would seem probable that the isomerization at the high temperatures used was more deep-seated than Merling had supposed.

1,4-Heptadiene, $CH_2{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3$.—Since the boiling point of this diolefin lies close to that of n-propyl alcohol, no attempt was made to separate the product from the reaction mixture as formed. After the refluxing had been continued for several hours, the condenser was replaced by a distilling tube and the diene together with a portion of propyl alcohol distilled off. The mixture began distilling at 83°, the temperature gradually rising to 94° when the distillation was stopped. This process of refluxing and distilling was continued until no more of the diolefin could be separated from the distillate upon dilution with water. One hundred grams of *a*-allyl-β-bromobutyl ethyl ether, 225 cc. of n-propyl alcohol and 100 g. of zinc dust yielded 37 g. of crude 1,4-heptadiene. After purification, as described above, there remained 23 g. of product having a boiling range of 90.2–92.6° of which 18 g. distilled at 92.0–92.3° at 755 mm.

TABLE V

1,4-DIOLEFINS

Diene	d_4^{20}	n^{20}	Boiling point, °C Observed	Literature
1,4-Penta	0.672	1.3880	28.5–29 2 (742 mm.)	29.5–31"[a]
1,4-Hexa	.6996	1.4162	64.3–64.6 (745 mm.)	64–66[b]
1,4-Hepta	.7176	1.4202	92.0–92.3 (755 mm.)	

[a] Dykstra, Lewis and Boord, Table I, Ref. a. [b] Griner, Ref. 6.

[9a] While this paper was being written for publication, an article by Kogerman on the "Synthesis of 1,4-Pentadiene," THIS JOURNAL, 52, 5060 (1930) has appeared. The author was unaware of our previous communication, ibid., 52, 3396 (1930), in which the same compound is described. Kogerman prepared 1,4-pentadiene in 15% yield by the action of allylmagnesium bromide on vinyl bromide. The work was evidently done with great care and the product obtained in almost exceptional purity. He gives the following physical constants: b. p. 25.8–26.2° at 756 mm., d_4^{20} 0.6594; n_D^{20} 1.3883; mol. refraction calcd., 24.26, found, 24.26.

[10] Griner, Ann. chim., [6] 26, 332 (1892).

[11] Merling, *Ann.*, 264,345 (1891).

Diolefin Tetrabromides

The tetrabromides of the diolefins were prepared by slowly adding bromine to a well-cooled solution of the hydrocarbon in chloroform. The reaction proceeded quite definitely in two steps; bromine was absorbed rapidly until approximately one-half of the required amount had been added; the remainder was absorbed more slowly. No attempt was made to isolate the intermediate diolefin dibromides.

1,4-Pentadiene Tetrabromide, $CH_2Br—CHBr-CH_2—CHBr\ CH_2Br$. -Eighteen grams of 1,4-pentadiene was dissolved in five times its volume of chloroform and the solution cooled in a freezing mixture. Bromine was added drop by drop until the solution maintained a permanent red coloration. The reaction mixture was placed under diminished pressure and the excess of bromine removed. Upon evaporation of the solvent the tetrabromide almost wholly solidified to a crystalline mass. After a third recrystallization from absolute alcohol, the product melted at 85.5 to 86°. The yield of purified product was 65%.

The oily residue from the crystals was filtered and distilled under diminished pressure. Analysis showed this liquid phase to be low in bromine.

1,4-Hexadiene Tetrabromide, $CH_3—CHBr—CHBr—CH_2—CHBr—CH_2Br$.—More difficulty was encountered in crystallizing 1,4-hexadiene tetrabromide. The viscous oil, free from chloroform, failed to crystallize at room temperature or in the ice-bath. Crystals were finally obtained by dissolving the liquid tetrabromide in absolute alcohol and chilling the solution in a bath of liquid ammonia. The crystals thus obtained were used to seed the remaining solutions cooled in a bath of ice and salt. After recrystallization, 8 g. of solid tetrabromide, m. p. 63.5–64°, was obtained together with 60 g. of the liquid isomer. The liquid tetrabromide was freed from volatile impurities by placing in a vacuum for four hours at a temperature of 40° and analyzing without further purification.

Griner[6] has described 1,4-hexadiene tetrabromide in three forms; the a-form melted at 182.3°, the β-form melted at 63–64' and the γ-form was a liquid which could not be distilled. The a-form was not obtained in the present work. Merling[11] gives the melting point of 1,4-hexadiene tetrabromide as 160–162° but his diolefin boiled 20° higher than the product herein described.

1,4-Heptadiene Tetrabromide, $CH_3—CH_2—CHBr—CHBr—CH_2—CHBr—CH_2Br$.—All attempts to crystallize this tetrabromide failed. When chilled in a liquid ammonia bath it solidified to a glass which melted completely upon removing from the bath. After volatile impurities had been removed in a vacuum, the product was analyzed without further purification. The yield was 97% on the basis of diolefin used. The physical characteristics and analyses of these 1,2,4,5-tetrabromo paraffins are shown in Table VI.

TABLE VI

1,4-DIOLEFIN TETRABROMIDES, $CH_2Br—CHBr—CH_2—CHBr—CHBr—R$

1,4-Diene	Physical state	M. p., °C.	d_4^{20}	n^{20}	Analysis, Br, % Calcd.	Found	
Penta	Solid	85.5–86"	...	....	82.44	82.58	82.56
	Liquid	......	...	....	82.44	79.16	
Hexa	Solid	63.5–64[b]	...	....	79.57	79.76	79.67
	Liquid	......	2.207	1.5833	79.57	79.36	79.31
Hepta	Liquid	......	2.091	1.5734	76.90	76.71	76.61

[a] Demjanow and Dojarenko, *Ber.*, 40, 2590 (1907), give 86°; Dykstra, Lewis and Boord, Table I, Ref. a, also give 86°. [b] Griner, Ref. 6, gives 64–66°.

Summary

By the use of allylmagnesium bromide the β-bromo ether synthesis of olefins has been extended to the preparation of 1,4-diolefins. 1,4-Pentadiene, 1,4-hexadiene and 1,4-heptadiene and the corresponding α-allyl-β-bromoalkyl ethers have been described.

The rule that unsaturated compounds with a double bond in the alpha position boil lower than the corresponding saturated hydrocarbons has been confirmed. It has been further shown that in any given family the continuous chain diolefins form a definite series with gradually increasing boiling points depending upon the relative position of the double bonds.

The 1,2,4,5-tetrabromo paraffins corresponding to the diolefins described have been prepared and found to show evidences of isomerism analogous to other polybromo aliphatic derivatives.

COLUMBUS, OHIO

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE OXIDATION OF METHANOL WITH AIR OVER IRON, MOLYBDENUM, AND IRON-MOLYBDENUM OXIDES

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RECEIVED JANUARY 10, 1931 PUBLISHED APRIL 6, 1931

The oxidation of methanol with air over various metal and oxide catalysts at 300 to 700° results in the formation of varying amounts of formaldehyde, carbon monoxide and carbon dioxide. Sabatier and more recently Lowdermilk and Day have given a review of the literature on this oxidation to which little need be added at this time.[1]

In 1926 a catalyst containing equal amounts of iron and molybdenum was found to be very efficient for the oxidation of methanol to formaldehyde.[2] The investigation described in this paper was initiated in order to correlate the characteristics of the iron–molybdenum catalyst with those of the catalyst containing only iron or molybdenum, with the hope of throwing some light upon the mechanism of the oxidation.

Catalysts. Molybdenum Oxide.—Five grams of ammonium molybdate and 4.5 g. of malic acid were dissolved in water and made ammoniacal with ammonium hydroxide.

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[1] Sabatier–Reid, "Catalysis in Organic Chemistry," Van Nostrand Company, New York, 1922, pp. 90--97; Lowdermilk and Day, THIS JOURNAL, 52, 3535 (1930).

[2] Homer Adkins and Virgil E. Meharg, in an application for a U. S. Patent (1927) assigned to the Bakelite Corporation. The authors of the present paper are indebted to Mr. Meharg and the Bakelite Corporation for the design of the very efficient washing tower and for the design and construction of the catalyst chamber, which were used in this investigation. The senior author is also grateful to Mr. Meharg for many pleasant associations and very valuable and willing cooperation while the former was temporarily employed by the Bakelite Corporation during the summer of 1926.

To this solution was added 60 cc. of three-sixteenths inch steel ball bearings, previously pitted with dilute hydrochloric acid and washed with distilled water until free of all acid. The solution was slowly evaporated almost to dryness with stirring. The steel balls, covered with the paste, were then poured onto a watch glass in layers of one thickness. The catalyst balls were further dried by placing in an oven at 60° for several hours.

Iron Oxide.—Three grams of iron reduced by hydrogen was added to a water solution of **6** g. of malic acid. The iron was almost completely dissolved by gently boiling the solution for three or four hours and the undissolved iron removed by decantation. The solution of ferrous malate was made ammoniacal by the addition of ammonium hydroxide. Sixty cubic centimeters of pitted steel ball bearings was added and the preparation of catalyst continued as described above.

Iron–Molybdenum Oxide.—One and one-fourth grams of iron reduced by hydrogen was added to a water solution of 4.5 g. of malic acid. The iron was almost completely dissolved by gently boiling the solution for three or four hours and the undissolved iron removed by decantation. To this solution of ferrous malate was added with stirring a water solution of **3 g.** of ammonium molybdate The combined solution was made ammoniacal by the addition of ammonium hydroxide, steel balls were added and the catalyst prepared as described above.

The catalysts thus prepared were placed in the aluminum reaction tube and decomposed in a slowly moving current of air for an hour or more at 360–375°. They were then ready for use.

Apparatus

The apparatus used in the experimental work is shown in Fig. 1 The air, which was supplied by a compressed air line **A,** was dried by passing it through a bottle B of concentrated sulfuric acid. The rate of flow of air was varied by means of a constant pressure valve. The flow of air was determined by means of a calibrated flowmeter C. The air was passed through a bottle D, containing the dried methanol. The vaporization of the alcohol was regulated by controlling the temperature of the vaporizer. The alcohol–air mixture was passed through a U-shaped aluminum catalyst tube. The U-

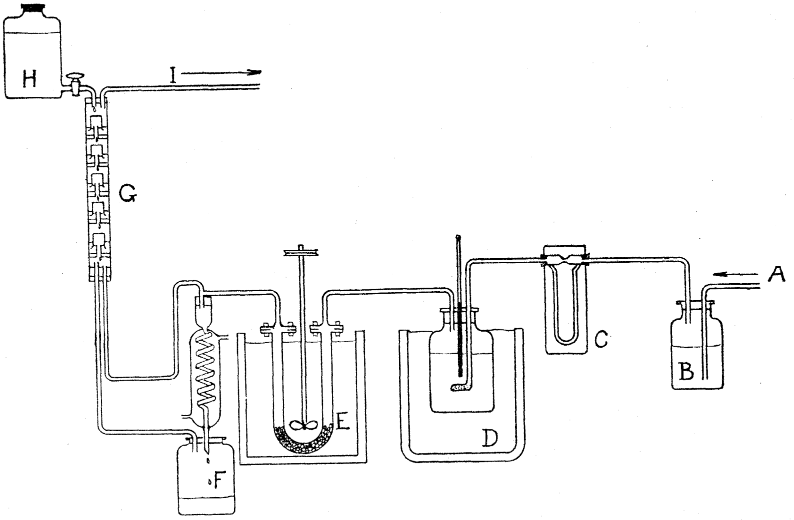

Fig. 3.—Apparatus for the oxidation of methanol.

tube was made of a flattened piece of aluminum tubing 75 cm. in length and 50 X 6 mm. (I. D.) in cross section. It was filled in the bottom and inlet side with glass rod and balls. A 15-cm. depth of catalyst was placed in the outlet side. The catalyst tube was immersed in an electrically heated bath (E) of sodium and potassium nitrates. The temperature of the bath was controlled by means of a Leeds and Northrup potentiometer controller. The products of the reaction were passed through a water-cooled coil condenser and then through a bubbling tower G 60 cm. in length, down which water was passed at the rate of about 100 ml. per hour from the reservoir H. All the formaldehyde and methanol in the gases were collected in the wash tower and flowed back through the condenser into bottle F. I is an exit tube for gaseous products leading to an Orsat apparatus.

Examination of Products.—The water-insoluble gaseous products were analyzed in an Orsat apparatus. The carbon dioxide was determined by absorption in potassium hydroxide solutions. The remaining oxygen was removed by yellow stick phosphorus. The carbon monoxide was removed by bubbling through an acid solution of cuprous chloride. The water-soluble products collected in bottle F were analyzed for formaldehyde by the method of Haywood and Smith.[3] The unreacted methanol was determined by oxidation with chromic acid.[4]

The percentage efficiency as used in this paper refers to the percentage of oxygen used in the conversion of methanol to formaldehyde and was calculated from gas analysis data in the following manner

$$\%\ \text{Efficiency} = \frac{\%\ \text{oxygen used} - (1.5 \times \%\ \text{carbon dioxide} + \%\ \text{CO})}{\%\ \text{oxygen used}}$$

The percentage efficiency so calculated agrees quite closely with the percentage efficiency calculated from the weight of formaldehyde obtained, the amount of methanol passed over the catalyst and the weight of methanol which was found unchanged in the distillate.

The Formation of **Methylal.**—Under certain conditions of operation formaldehyde reacts with methanol in the catalyst chamber with the formation of the methyl acetal of formaldehyde. The compound is only partially condensed with the other liquid products and some escapes with the gaseous products of the reaction. This acetal is not at all readily hydrolyzed. The method of Lowdermilk and Day[5] for the determination of unchanged methanol may give quite inaccurate results because methylal would appear with methanol in their procedure for analysis. The presence of methylal among the reaction products may be suspected if there is a 0.5 to 2% reduction in the volume of the effluent gas when bubbled through sulfuric acid, or if there is a discrepancy between the efficiency as calculated from the gas analysis and from the formaldehyde and methanol in the distillate. Methylal was formed in considerable quantities in one series of experiments, apparently due to the accumulation of alumina on the walls of the catalyst chamber. No further difficulty was experienced after the chamber had been thoroughly cleaned with a sodium hydroxide solution and with hydrochloric acid. Methylal was also formed when rather completely oxidized aluminum turnings were used as a support for the catalysts.

General Procedure.—The catalyst was put in place and decomposed and methanol and air passed over it continually (except for the removal of samples) for several days or weeks. Two or three times during each twenty-four hours the passage of the reactants was stopped and the amount of methanol which had been passed over the catalyst de-

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[3] Haywood and Smith, THIS JOURNAL, 27, 1185 (1905)

[4] Blank and Finkenbeiner, *Ber.*, **39,1327** (1906).

[5] Lowdermilk and Day, THIS JOURNAL, 52, **3537** (1930).

termined by weighing the methanol left in the vaporizer. The condensate was taken out of the receiver and made up for analysis. Gas analyses were made from time to time on the effluent gases. The temperature of the catalyst and amount and ratio of air and methanol were changed as desired. After a given variation in the conditions of reaction had been studied, the conditions were again made standard, *i. e.*, 93 liters of air and 9 g. of methanol per hour at 373° and assurance was obtained that the catalyst had not been permanently modified. In this way a given sample of catalyst could be used for several weeks for the study of a variety of experimental conditions. Duplicate preparations of catalyst were used in the testing of all important points. The catalyst can be readily and precisely duplicated. Preparations made and tested independently by the two authors gave results which agreed almost as well as the data for the three typical experiments given below: 1–2–3. Iron–molybdenum oxide, 373°, 93 liters of air, 8.9, 9.38, 8.97 g. of methanol per hr., % converted to formaldehyde as actually obtained, 91.6, 91.8, 90.3%; % recovered methanol, 5.03, 6.47, 5.6 g. Gas analysis: % CO_2, 0.1, 0.1, 0.1; % oxygen, 18.0, 18.0, 17.5; % CO, 0.1, 0.1, 0.2; % efficiency based on gas analysis, 93, 93, 91.

Statement of Experimental Results

Space is not available for the tabulation of the complete data of the more than a hundred experiments upon the oxidation of methanol over oxide catalysts which have been carried on in the course of this investigation. It must suffice to give the following abstract of these data.

The characteristics of a molybdenum oxide catalyst as concluded from a study of its behavior toward oxidation of methanol with air to formaldehyde were found to be as follows.

1. The catalyst was highly efficient as evidenced by the fact that all of the methanol which was oxidized was converted into formaldehyde with no formation of the oxides of carbon.

2. The activity of the catalyst decreased during the first twenty-four hours of use, after which a steady state was reached in which its activity was approximately constant for several days. For example, a molybdenum oxide catalyst was capable of causing the oxidation of 6.8 g. of methanol (57.8% yield) to formaldehyde per hour during its first five hours of use; 5.17 g. of methanol (48.6%) to formaldehyde per hour for three and one-half hours after being used for five hours; and 4.73 g. of methanol (45.9%) to formaldehyde per hour the next three and one-half hours as compared to a 35.5% yield under comparable conditions after the steady state was reached.

3. The amount of methanol oxidized to formaldehyde per hour was a linear function of the rate of passage of the methanol over the catalyst. When 2.26, 5.28, 12.95, 18.4 and 20.0 g. of methanol per hour was passed over the catalyst with 50 or 93 liters of air, 1.58, 2.25, 3.72, 4.93 and 5.36 g. of the methanol, respectively, was converted into formaldehyde. However, the amount of methanol oxidized to formaldehyde per hour did not increase (over the range investigated) with increase in the rate of passage of the air over the catalyst. When 6.17 g. of methanol and

136 liters of air were passed over the catalyst in an hour, 2.31 g. of the methanol was converted into formaldehyde, as compared to the conversion of 2.41 g. of methanol when 6.67 g. of methanol in 50 liters of air were passed over the catalyst.

4. The percentage conversion of methanol to formaldehyde rose with decrease in the rate of passage of the methanol over the catalyst. When 20.0, 10.2, 6.67 and 2.57 g. of methanol were passed over the catalyst with 50 liters of air, the yields were 26.9, 33.3, 36.2 and 54.2%, respectively.

5. The conversions of methanol to formaldehyde at 373, 390 and 400° were approximately the same. However, at 361° lower conversions were obtained. When approximately 9.5 g. of methanol in 93 liters of air was passed over the catalyst at 361, 373, 390 and 400°, yields of 23.8, 31.5, 32.1 and 32.4%, respectively, were obtained when the catalyst had reached its "steady state."

The characteristics of an iron oxide catalyst, as concluded from a study of its behavior when methanol mixed with air was passed over it, were found to be as follows.

1. The catalyst was very active, the methanol being oxidized almost wholly to carbon dioxide. When the amount of methanol passed over the catalyst was varied from 11.2 to 33 g. per hour (373°, 93 liters of air per hour), there were only traces of formaldehyde and this only with a catalyst that had been in operation for several days and with more methanol passing over the catalyst than could be oxidized to carbon dioxide by the available oxygen.

2. The activity of the catalyst became less as the temperature of the reaction was lowered and increased as the temperature was raised. At 310°, with 20 g. of methanol and 93 liters of air, 9.4% of the methanol passed over the catalyst was converted to formaldehyde; 81.0% remained unreacted, the remaining 9.6% having been converted into carbon dioxide. At 340° approximately 18% of the methanol was converted into formaldehyde, with about 68% remaining unreacted; the remaining 14% was converted into carbon dioxide. At 400 or 443°, no formaldehyde was formed, 4.92% of the methanol remained unreacted, the remainder having been lost as oxides of carbon.

3. An iron oxide catalyst that has been used at a low temperature (340°) when raised to 373° was less active toward oxidizing methanol and produced more formaldehyde than it formerly did at 373°. It gradually recovered its original activity, giving results identical within experimental error with those obtained previously at 373°. Previous to the lowering of the temperature, the results obtained at 373° showed the formation of 1.3% of formaldehyde with very little methanol (5.1%) remaining unreacted. After raising the temperature again to 373°, the results obtained for the first two experiments showed conversions

of methanol to formaldehyde of 4.67 and 4.16%, respectively; the amounts of methanol remaining unreacted were 21 9 and 7.88%, respectively.

The characteristics of an iron–molybdenum oxide catalyst, as concluded from a study of its behavior when methanol was oxidized with air on the surface of the catalyst, were as follows.

1. The activity and efficiency of the catalyst increased during the first few hours of use, after which a steady state was reached in which its activity was constant for weeks. During the first twelve hours of use, the average conversion of methanol to formaldehyde was 82.0%. During the next five hours, the average conversion was 88.5%, and for the next six and one-half hours, the average conversion was 90.8%. The air flow was kept at 93 liters per hour, while the passage of methanol varied from 8.8 to 10.1 g. per hour in these experiments.

2. More carbon monoxide than dioxide was produced from methanol over molybdenum–iron oxide catalysts.

3. The iron–molybdenum oxide catalyst was relatively inactive toward formaldehyde. A 5-cm. depth of catalyst produced the same yield of formaldehyde as did a 15-cm. depth of catalyst using 93 liters of air per hour carrying approximately 10 g. of methanol per hour. The efficiency for the 5-cm. depth of catalyst was 92.3% and for the 15-cm. depth 85.6%. The above conclusion may also be drawn from the results obtained by passing alcohol and air in the same ratio but at different rates over a 15-cm. depth of catalyst. Considering air flows of 93 and 136 liters per hour, the efficiencies were found to be 90.7 and 93.8%, respectively. However, with an air flow of 50 liters per hour, the yield (80.8%) as well as the efficiency (66.5%) decreased considerably. The "space-time-velocities" in passing 136 and 50 liters of air over a 15-cm. depth of catalyst were the same as for the passage of 93 liters of air over 10.3 and 27.9-cm. depths of catalyst, respectively.

4. Increasing the rate of passage of methanol increased the grams of methanol oxidized to formaldehyde, but there was also a decrease in efficiency if the methanol passage became too high. With 93 liters of air carrying 9.38 g. and 15.0 g. of methanol per hour, the weight of methanol converted to formaldehyde was 8.61 and 12.8 g., respectively. The efficiencies were 90.7 and 85.5%, respectively.

5. The maximum activity was obtained when equimolecular proportions of iron and molybdenum were present in the oxide mixture. A high percentage of iron oxide in the catalyst showed more of the carbon dioxide forming properties of an iron oxide catalyst, while a high percentage of molybdenum oxide in the catalyst showed properties intermediate between those of an iron–molybdenum oxide catalyst and a molybdenum oxide catalyst, that is to say, the efficiency was higher and the conversion of methanol to formaldehyde was lower than for the mixed oxide catalyst.

6. Lower conversion of methanol to formaldehyde was obtained at 353 than at 373 and at 400°. The efficiency was less at 400 than at 373 and 353°. With 93 liters of air and approximately 9 g. of methanol passing over the catalyst per hour, the conversions of methanol to formaldehyde at 353, at 373 and at 400° were 85.2: 91.8 and 91.9%, respectively, and the efficiencies were 90.0, 90.7 and 85.3%, respectively.

Discussion of Results

The catalyst surface of these oxide catalysts was constantly undergoing change as measured by the amount of oxidation of methanol or by the ratio of products. For example, in the case of molybdenum oxide a new catalyst rapidly decreased in activity for several hours until a steady state was reached for the particular temperature, rate and ratio of methanol and air involved. The new iron and iron–molybdenum catalysts showed a change in the ratio of products during several hours before a steady state was reached. When the experimental conditions were changed the catalysts rather slowly shifted in activity until a new steady state was reached. The former steady state could be slowly regained if the experimental conditions which produced it were reproduced. The constant change and renewal of the active surface was also indicated by the fact that the catalysts are active for weeks and months of continuous use. It is extremely unlikely that any surface would remain active for any such lengths of time unless it was being continually renewed. Thus the relationship between an effective catalyst and the reactants must not only be such that the former brings about the reaction of the latter, but the reactants must maintain the state of the catalyst which is favorable to the desired reaction.

A desirable catalyst for the oxidation of methanol to formaldehyde would therefore be one that required only a low concentration of methanol in the effluent gas stream in order to maintain it in the optimum state of reduction; in other words, a desirable catalyst would be one which would stay reduced without an excess of methanol. It should not be active toward formaldehyde, that is, it should desorb it rapidly. Molybdenum oxide is an efficient but undesirable catalyst because too much methanol is required to keep it reduced to the active state. Iron oxide is an undesirable catalyst because it goes into such a high state of oxidation that any formaldehyde formed is not desorbed, but is oxidized to carbon dioxide. The mixture of iron and molybdenum oxide apparently requires no considerable excess of methanol to maintain it in the desired state of oxidation and has a low activity toward formaldehyde. The mixture of oxides differs from either of the pure oxides not only in these facts but in that the mixture produces the monoxide rather than the dioxide of carbon.

Langmuir[6] in his classical paper on the oxidation over platinum of carbon monoxide by oxygen, pointed out that there are three possible mechanisms for such an oxidation: (1) the oxygen may be absorbed by the platinum and then be struck by a molecule of carbon monoxide; (2) the carbon monoxide may be absorbed by the platinum and then be struck by a molecule of oxygen; (3) the two reactants may be adsorbed on adjacent active points on the catalyst surface sufficiently close together so that the reaction may ensue.

Oxidation of methanol on the basis of cases (1) and (3) involves successive addition and removal of oxygen from the catalyst, the difference between the two cases being as to whether the methanol reacts from the vapor state or from the adsorbed state. The adsorbed oxygen postulated in both cases might be adsorbed on the catalyst or might be held as a so-called definite oxide. For the purpose of the discussion that follows, it is immaterial which is the case.

If either case (1) or (2) holds for the oxidation of methanol over molybdenum oxide, then it should be possible by using a proper ratio of reactants either to consume almost all of the oxygen or convert almost all of the methanol to formaldehyde. The experimental results very definitely show that this is not true, as the percentage conversion of methanol to formaldehyde cannot be raised very high no matter how much the excess of oxygen or how long the time of contact, *i. e.*, how slowly the reactants are passed over the catalyst. The amount of methanol oxidized per hour is a linear function of the amount of methanol passed over the catalyst for a 10-fold increase in rate of passage. No more than 10% of the total available amount of oxygen could be consumed no matter how large the excess of methanol. It is probable, therefore, that the two reactants must both be adsorbed on adjacent active points on the surface of the catalyst before reaction may ensue.

Summary

The characteristics of molybdenum oxide, iron oxide and a mixed iron–molybdenum oxide catalyst as displayed in the catalysis of the oxidation of methanol with air have been described. In brief it may be said that molybdenum oxide was 100% efficient for the oxidation of methanol to formaldehyde, since this is the only reaction which occurred. However, only about 38% of the methanol could be converted to formaldehyde. Iron oxide was a very active catalyst but it induced the formation of carbon dioxide almost exclusively. A catalyst containing equal atomic amounts of iron and molybdenum converted over 90% of the methanol passed over it into formaldehyde, the other product being carbon monoxide. It is thus by far the best catalyst, so far described, for the oxidation

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[6] Langmuir, Trans. *Faraday Soc.*, 17, 3, 653 (1922).

of methanol. The catalyst was quite stable and may be used continually for months.

At least in the case of molybdenum oxide there is evidence that the reaction between methanol and oxygen takes place when both reactants are on the surface of the catalyst.

Evidence has been presented which indicates that the catalyst surface of these oxide catalysts is continually renewed during use; therefore the relationship between an effective catalyst and the reactants must not only be such that the former brings about the reaction of the latter, but the reactants must maintain the catalyst in the state of oxidation which is favorable to the desired reaction.

MADISON, WISCONSIN

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE EFFECT OF COPPER UPON THE YIELDS OF GRIGNARD REAGENTS

BY GEORGE JOHNSON AND HOMER ADKINS

RECEIVED JANUARY 10, 1931 PUBLISHED APRIL 6, 1931

It is well known that the reaction of alkyl halides and magnesium results in the formation of Grignard reagents and of hydrocarbons, as indicated in equations I and II.

$$RX + Mg = RMgX \qquad (I)$$

$$2RX + Mg = R_2 + MgX_2 \qquad (II)$$

There has been in progress for some time in this Laboratory a study of the factors which determine the ratio of these two competitive reactions. During the course of this investigation some observations have been made in regard to the effect of copper upon the ratio of the reaction products which are of such practical importance that it seems desirable to publish them in advance of a more comprehensive paper, especially in view of the results of Gilman, Peterson, Schultz and Heck,[1] who reported that magnesium in certain copper–magnesium alloys reacted more rapidly with alkyl halides than did pure magnesium. Upon the basis of these findings it seemed that the use of the alloy might be advantageous in the preparation of Grignard reagents and this practice has been followed by a number of investigators.

The determination of the effect of various experimental conditions upon the ratio of the Grignard and Wurtz reactions was made in the following manner. The apparatus used was essentially of the type and size described and used by Gilman and Meyers for the preparation of ethyl-

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Gilman, Peterson and Schulze, Rec. *trav. chim.*, 47, 22 (1928); Gilman and Heck, *Bull. soc. chim.*, 45,250 (1929).

magnesium iodide,[2] except that a detachable side-arm buret was connected to the outer end of the siphon tube passing through the wall of the flask. The desired quantity of magnesium was introduced into the reaction flask and the apparatus assembled. The flask and attached condenser were then swept out with dry hydrogen while the sample of alkyl halide was being weighed. After discontinuing the flow of hydrogen, from 10 to 15 ml. of anhydrous ether was introduced from the attached 60-ml. separatory funnel. The alkyl halide, contained in a 50-ml. glass-stoppered flask, was diluted with about 20 ml. of anhydrous ether, quickly transferred to the dropping funnel, after which approximately 15 ml of ether, in two or three portions, was used to wash out any remaining sample from the bottle, and all washings rapidly transferred to the dropping funnel. This diluted the sample to a volume of 35 to 40 ml. The contents of the flask were then stirred and the alkyl halide introduced dropwise over a period of thirty-five to forty minutes. A reaction, evidenced by the boiling of the solution, usually set in after one to three minutes. After the halide was all introduced, stirring was continued for five minutes, or longer if boiling continued, and a further quantity of about 50 ml. of dry ether was then introduced through the dropping funnel, over a period of ten to fifteen minutes, so as to bring the total volume up to approximately 105 ml. Dry hydrogen gas was then bubbled through the reaction mixture for two or three minutes, after which the stirring was stopped, all openings to the reaction flask corked to exclude air, and the reaction mixture allowed to stand undisturbed for one-half hour, or until all solid matter had settled. Making due allowance for the stirring rod and any other residual solid matter, the total volume of the reaction mixture was then obtained from the graduated scale on the neck of the flask, and three aliquots of approximately 20 ml. each were forced out under hydrogen pressure through the siphon tube into the buret.

The acid titration method, as recommended by Gilman, Wilkinson, Fishel and Meyers,[3] was used for the estimation of the Grignard reagent produced, Each 20-ml. aliquot was drained from the buret into 50 ml. of water, an excess of 0.2 N sulfuric acid added and the product heated on the steam-bath to accelerate hydrolysis and to expel the ether. The resulting solution was then cooled, and the sample titrated with 0.1 N sodium hydroxide, using phenolphthalein as an indicator. From these data the amount of $Mg(OH)X$ present in the mixture was calculated and hence the yield of $RMgX$.

The magnesium (88%) copper (12%) alloy used in this investigation was in the form of turnings and was supplied by the Dow Chemical Company. Powdered copper alloy from the Eastman Kodak Company was

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[2] Gilman and Meyers, THIS JOURNAL, 45, 159–165 (1923).

[3] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, 45, 150 (1923).

also used, as was pure magnesium turnings plus copper powder ("Natur Kupfer C"). The results obtained with the powder were not greatly different from those obtained with magnesium turnings. Copper powder reduced the yield of Grignard reagent but not so markedly as when the metal was alloyed with the magnesium. In the case of four of the halides only a small excess of magnesium was used over that necessary for the formation of the Grignard reagent. In the case of cyclohexyl bromide and allyl bromide a considerable excess of magnesium was used because Gilman and McGlumphy[4] reported that the yield of Grignard reagent from allyl bromide was higher when a large excess of magnesium was used. Ethyl iodide was used both with a small and large excess of magnesium.

TABLE I

THE EFFECT OF COPPER UPON THE YIELD OF GRIGNARD REAGENTS[a]

Alkyl halide		Magnesium,	% yield of RMgX	
Name	Moles	g. atoms	From Mg	From Cu–Mg
n-Butyl bromide	0.056	0.062	92.5	78.7 ± 2 (3)
Sec.-butyl bromide	.059	.062	73.8	49.6
n-Butyl iodide	.057	.058	82.4	64.2
Ethyl iodide	.059	.062	83.4	76.1
Ethyl iodide	.058	.250	90.8	80.7
Benzyl chloride	.059	.065	94.1 ± 0 (2)	80.2 ± 2 (8)
Cyclohexyl bromide	.059	.165	82.5 ± 2 (3)	64.711 (3)
Allyl bromide	.058	.272	72.1 ± 4 (10)	6.014 (6)
Phenyl bromide	.059	.063	90.8 ± 0.5 (3)	89.1 ± 2 (3)

[a] Three analyses were made on each reaction mixture. When more than one reaction mixture was made up the numbers as well as the variation in yields are indicated in the table.

There are given in Table I the yields of Grignard reagents obtained for eight halides through their reactions with magnesium and the copper magnesium alloy. It is apparent from the data so reported that copper lowers the yield of Grignard reagent. The halides in the order of their increasing susceptibility to the effect of copper were phenyl bromide, ethyl iodide, benzyl chloride, n-butyl bromide, n-butyl iodide, cyclohexyl bromide, *sec.*-butyl bromide and allyl bromide. The formation of the Grignard reagent from the first of these was little affected by copper, while in the case of allyl bromide the yield of the reagent was lowered to 10% of the value obtained with pure magnesium.

Meisenheimer[5] ascertained the ratio of reactions I and II by comparing the amount of Grignard reagent with the total amount of halogen in the ether solution which was precipitable as silver halide. If no Wurtz reaction had occurred, the ratio of precipitable halogen to the Grignard reagent would be 1 to 1. If the Wurtz reaction had occurred, then the

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[4] Gian and McGlumphy, Bull. *soc. chim.*, 43, 1322 (1928).

[5] Meisenheimer, *Ber.*, 61, 708 (1928).

ratio of halogen to Grignard reagent would be greater than 1 to 1 by a corresponding amount. For example, if the two reactions had occurred to an equal extent, the ratio would be 2 to 1.

There is given below after the name of each halide the amount of precipitable halogen, for one part of Grignard reagent, which was found for pure magnesium and for magnesium–copper alloy: benzyl chloride, 1.02 (Mg); 1.20 (Mg-Cu); cyclohexyl bromide 1.20 (Mg), 1.52 (Mg–Cu); n-butyl bromide 1.08 (Mg), 1.26 (Mg–Cu); *sec.*-butyl bromide 1.33 (Mg), 1.98 (Mg–Cu); n-butyl iodide 1.21 (Mg), 1.54 (Mg–Cu); ethyl iodide 1.20 (Mg) 1.27 (Mg–Cu), phenyl bromide 1.1 (Mg), 1.1 (Mg–Cu); and allyl bromide 1.35 (Mg). These figures show very definitely that copper promotes the Wurtz reaction. The ratio is without significance in the case of magnesium-copper alloy and allyl bromide because so much magnesium bromide was formed that the solubility of its etherate was exceeded,[6] and so was not found upon analysis of the ether solution.

The completeness of reaction of each alkyl halide with magnesium may also be determined from the amount of halogen in the ether solution which was precipitable as silver halide. Upon this basis from 98 to 100% of the phenyl, n-butyl, *sec.*-butyl and cyclohexyl bromide and n-butyl and ethyl iodide and from 94 to 98% of the benzyl chloride underwent reaction over both pure magnesium and the alloy. In the case of allyl bromide, from 96 to 98% of the halide underwent reaction with pure magnesium, while with magnesium–copper alloy so much magnesium bromide was formed that the solubility of its etherate was exceeded, as noted above.

No attempt has been made during this investigation to determine accurately the rates of reaction of the alkyl halide; however, there has been no evidence that the halides reacted more rapidly with the alloy than with pure magnesium. In fact, in some cases the reaction started more slowly with the alloy than with the pure magnesium.

Summary

The yields of Grignard reagents obtained by reacting eight alkyl halides with magnesium and with an alloy of magnesium and copper have been determined. The yields of the Grignard reagent were very considerably lowered, except from phenyl bromide, by the presence of the copper, which promoted the competitive Wurtz reaction.

MADISON, WISCONSIN

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[6] *Cf.* Evans and Rowley, THIS JOURNAL, 52, 3523 (1930).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REDUCTION OF AZOBENZENE, AZOXYBENZENE AND NITROSOBENZENE BY THE SYSTEM MAGNESIUM + MAGNESIUM IODIDE

BY W. E. BACHMANN

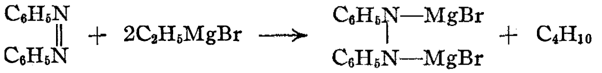
RECEIVED JANUARY 10, 1931 PUBLISHED APRIL 6, 1931

Previous papers[1] have described the addition of the MgI group to the C=O group of various classes of compounds and to the trivalent C atom of triarylmethyls, the addition taking place when these compounds are treated with a mixture of magnesium and magnesium iodide in an ether-benzene solution. According to the hypothesis which was set forth, the active reducing agent is magnesium subiodide, generated by the interaction of the metal and metal halide

$$Mg + MgI_2 \leftrightarrows 2MgI \qquad (1)$$

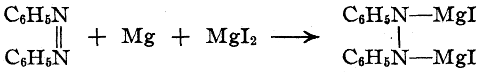
and present as such only in minute quantities at any one moment.

The behavior of the mixture, Mg + MgI_2, with azobenzene was of particular interest in view of the mechanism of the reduction of azobenzene by the Crignard reagent. Franzel and Deibel[2] found that ethylmagnesium bromide reduces azobenzene to a hydrazobenzene derivative and they formulated the reaction as follows



$$\begin{matrix} C_6H_5N \\ \| \\ C_6H_5N \end{matrix} + 2C_2H_5MgBr \longrightarrow \begin{matrix} C_6H_5N\text{—}MgBr \\ | \\ C_6H_5N\text{—}MgBr \end{matrix} + C_4H_{10} \qquad (2)$$

Addition of water gives hydrazobenzene.[3] It is observed that the reduction of the azobenzene is occasioned by the addition of the MgX group of the Grignard reagent to each of the nitrogen atoms of the N=N group. It was, therefore, to be expected that the binary system, in virtue of its ability to furnish MgX, would readily accomplish a similar reduction. Such was found to be the case. A mixture of magnesium and magnesium iodide reduces azobenzene rapidly and completely according to the following reaction



$$\begin{matrix} C_6H_5N \\ \| \\ C_6H_5N \end{matrix} + Mg + MgI_2 \longrightarrow \begin{matrix} C_6H_5N\text{—}MgI \\ | \\ C_6H_5N\text{—}MgI \end{matrix} \qquad (3)$$

I

For each gram molecule of azobenzene, a gram atom of magnesium is dissolved and a gram molecule of iodomagnesium-hydrazobenzene (I) is formed. In the process of reduction the solution displays a series of intense colors, brown, reddish-brown and brown-black; at the end of the

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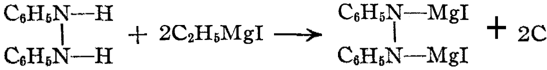
[1] See Gomberg and Bachmann, THIS JOURNAL, 52, 4967 (1930), for principal references.

[2] Franzel and Deibel, *Ber.*, 38, 2716 (1905).

[3] See also Gilman and Pickens, THIS JOURNAL, 47, 2406 (1925); and Rheinboldt and Kirberg, J. prakt. *Chem.*, **118**, 1 (1928).

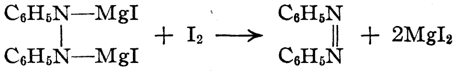
reaction the mixture is colorless. The play of colors is probably due to the formation of a complex between the iodomagnesium-hydrazobenzene and unreduced azobenzene, the complex being analogous to the quinhydrone-like compound which Schlenk and Appenrodt[4] obtained by the action of sodium or potassium on azobenzene. They found that only one atom of potassium reacted for each molecule of azobenzene and they considered their dark violet-brown product to have the composition, $C_6H_5(K)N{-}N(K)C_6H_5{\cdot}C_6H_5N{=}NC_6H_5$. Unlike sodium and potassium, the binary system is able to reduce the complex completely to the hydrazobenzene derivative. The identity of the product (I) as iodomagnesium-hydrazobenzene was established by its reactions and by its synthesis from hydrazobenzene through the action of a Grignard reagent.



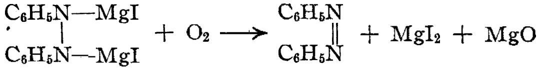
$$\begin{array}{c} C_6H_5N{-}H \\ | \\ C_6H_5N{-}H \end{array} + 2C_2H_5MgI \longrightarrow \begin{array}{c} C_6H_5N{-}MgI \\ | \\ C_6H_5N{-}MgI \end{array} + 2C_2H_6 \qquad (4)$$

The iodomagnesium-hydrazobenzene (I) is very reactive. It is instantly decomposed by water into hydrazobenzene. The yield of hydrazobenzene obtained by hydrolysis of the reaction mixture varies between 85 and 90% of that calculated according to Equation **3.** The remainder of the product consists of aniline produced by reduction beyond the hydrazobenzene stage; in agreement with this result is the fact that the amount of magnesium dissolved in the reaction is 10 to 15% greater than that required by Equation **3.**

Iodine and oxygen react readily with the iodomagnesium-hydrazobenzene; the principal product of the reactions is azobenzene.

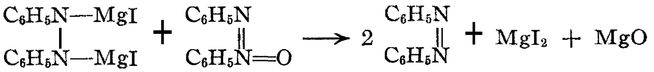


$$\begin{array}{c} C_6H_5N{-}MgI \\ | \\ C_6H_5N{-}MgI \end{array} + I_2 \longrightarrow \begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N \end{array} + 2MgI_2 \qquad (5)$$



$$\begin{array}{c} C_6H_5N{-}MgI \\ | \\ C_6H_5N{-}MgI \end{array} + O_2 \longrightarrow \begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N \end{array} + MgI_2 + MgO \qquad (6)$$

If an equivalent amount of azoxybenzene is added to the reduction product, the latter is oxidized and the azoxybenzene is reduced to one and the same product, azobenzene



$$\begin{array}{c} C_6H_5N{-}MgI \\ | \\ C_6H_5N{-}MgI \end{array} + \begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N{=}O \end{array} \longrightarrow 2 \begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N \end{array} + MgI_2 + MgO \qquad (7)$$

This reaction is analogous to the reaction between iodomagnesium-hydrobenzoinate and benzil, which yields benzoin as the sole product.[5]

The iodomagnesium-hydrazobenzene reacts with benzoyl chloride, both MgI groups being replaced by benzoyl groups with the formation of dibenzoyl-hydrazobenzene. It reacts with carbon dioxide in the manner of a Grignard reagent giving the iodomagnesium salt of hydrazobenzene-N,N-dicarboxylic acid.

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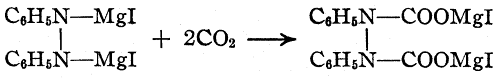
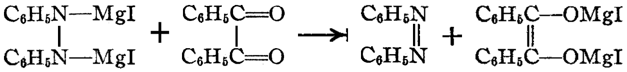
[4] Schlenk and Appenrodt, *Ber.*, 47,4851 (1914).

[5] Shankland and Gomberg, THIS JOURNAL, 52,4973 (1930).



$$\begin{array}{c} C_6H_5N\text{—}MgI \\ | \\ C_6H_5N\text{—}MgI \end{array} + 2CO_2 \longrightarrow \begin{array}{c} C_6H_5N\text{—}COOMgI \\ | \\ C_6H_5N\text{—}COOMgI \end{array} \qquad (8)$$

Benzil is able to abstract both MgI groups from the nitrogen atoms and attach them to its two C=O groups

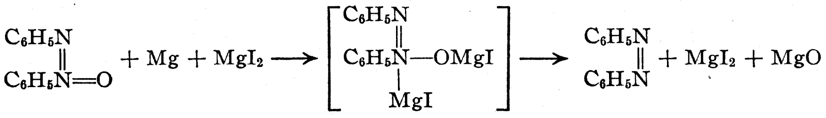


$$\begin{array}{c} C_6H_5N\text{—}MgI \\ | \\ C_6H_5N\text{—}MgI \end{array} + \begin{array}{c} C_6H_5C{=}O \\ | \\ C_6H_5C{=}O \end{array} \longrightarrow \begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N \end{array} + \begin{array}{c} C_6H_5C\text{—}OMgI \\ \| \\ C_6H_5C\text{—}OMgI \end{array} \qquad (9)$$

On hydrolysis azobenzene and benzoin[6] are obtained in equivalent amounts. Benzaldehyde, however, behaves differently; it gives benzanilide as the chief product.

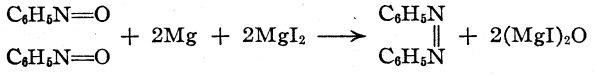
Para-substituted dimethyl-, dimethoxy- and diphenylazobenzene were reduced by the binary system; in all cases reduction occurred to a considerable extent (up to 49%) beyond the hydrazobenzene stage and an equivalent amount of the corresponding substituted aniline was found in the hydrolyzed products. The actual mechanism of this reduction to the aniline stage is unknown.

Azoxybenzene and substituted azoxybenzenes were found to react rapidly with a mixture of magnesium and magnesium iodide. If only one gram atom of metallic magnesium is employed for a gram molecule of azoxybenzene, azobenzene is obtained on hydrolysis of the reaction product. If twice that amount of reducing agent is present, reduction proceeds to iodomagnesium-hydrazobenzene. One may consider that the azoxybenzene is reduced to azobenzene (Equation 10) and that this is then reduced further according to Equation 3.



$$\begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N{=}O \end{array} + Mg + MgI_2 \longrightarrow \left[\begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N\text{—}OMgI \\ | \\ MgI \end{array}\right] \longrightarrow \begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N \end{array} + MgI_2 + MgO \qquad (10)$$

The reaction between nitrosobenzene and a mixture of magnesium and magnesium iodide is similar to the reduction of azobenzene and azoxybenzene. The principal reaction (to the extent of 70%) consists in the reduction of nitrosobenzene to azobenzene (Equation 11) followed by the reduction of the latter compound to iodomagnesium-hydrazobenzene.



$$\begin{array}{c} C_6H_5N{=}O \\ \\ C_6H_5N{=}O \end{array} + 2Mg + 2MgI_2 \longrightarrow \begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N \end{array} + 2(MgI)_2O \qquad (11)$$

When an amount of reducing agent corresponding to that given in Equation 11 is employed, azobenzene is the chief reduction product. By using an excess of reducing agent, iodomagnesium-hydrazobenzene is obtained.

Nitrosobenzene can also be reduced by iodomagnesium-hydrazobenzene; both reactants are converted to azobenzene in the reaction.

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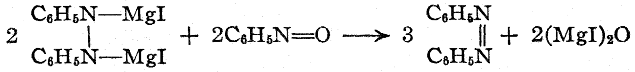
[6] Compare the reduction of benzil by Mg + MgI_2, Gomberg and Bachmann, This Journal, 49, 2584 (1927).



$$2\begin{matrix} C_6H_5N—MgI \\ | \\ C_6H_5N—MgI \end{matrix} + 2C_6H_5N{=}O \longrightarrow 3\begin{matrix} C_6H_5N \\ \| \\ C_6H_5N \end{matrix} + 2(MgI)_2O \qquad (12)$$

Experimental

For rapid reaction magnesium was used in the form of powder or turnings; when magnesium powder was employed, the reaction was completed in several hours. In most cases magnesium rods were used because they can be withdrawn from the solution at any time and the weight of magnesium that has reacted can be accurately determined. Best results were obtained when the reaction was carried out at room temperature. Moisture, oxygen and carbon dioxide must be excluded from the reaction mixture; this was accomplished most conveniently by carrying out the reaction in stoppered glass cylinders or heavy test-tubes of such a capacity that the solutions practically filled the tube.

Reduction of Azobenzene.—To a filtered solution of magnesium iodide, prepared from 27 g. of iodine in a mixture of 40 cc. of ether and 80 cc. of benzene, was added 18.2 g. of azobenzene and a rod of magnesium. The tube was quickly stoppered and shaken mechanically at room temperature. Frequently the reaction started in a few minutes, as was evidenced by the appearance of a dark brown color. During the reduction the solution became dark brown, reddish-brown and brown-black (like dark-oak stain) in color. The color gradually disappeared and after two days the mixture was practically colorless and contained a large amount of finely-divided grayish-white solid. The magnesium rod was withdrawn from the mixture, washed with alcohol and weighed. The loss in weight was 2.70 g., which is 111% of that calculated (2.43 g.) according to Equation 3 Numerous determinations showed that from 10–15% reduction occurred beyond the hydrazobenzene stage.

The mixture was poured into ice and water that had been saturated with carbon dioxide, and all subsequent operations were carried out in an atmosphere of carbon dioxide in order to prevent oxidation. Dilute acetic acid was used to dissolve the magnesium hydroxide which was produced on hydrolysis. After the ether–benzene solution had been washed with water, the solvents were removed by distillation under reduced pressure at 30–35° (at high temperatures hydrazobenzene is decomposed into azobenzene and aniline). The solid residue was treated with warm petroleum ether in order to remove azobenzene and aniline; the insoluble colorless residue of hydrazobenzene weighed 14.7 g. The petroleum ether filtrate was evaporated to dryness under reduced pressure and the residue was treated with a cold solution of 30% acetic acid in order to extract aniline; this acid extract yielded 1.2 g. (6%) of aniline. The residue which was insoluble in acetic acid was heated with dilute hydrochloric acid in order to convert the hydrazobenzene in it to benzidine. The azobenzene which remained weighed 0.25 g. (1%) and the benzidine (isolated as sulfate) corresponded to 1.6 g. of hydrazobenzene, The total weight of hydrazobenzene was 16.3 g. (89%) and agrees with that expected from the amount of magnesium that had reacted.

Attempts were made to reduce the product more completely to aniline by employing an excess of magnesium and magnesium iodide and allowing a long period of time for the reaction. The results were no different from those given above.

It is possible to reduce a gram molecule of azobenzene completely without using a full mole of magnesium iodide; this indicates that magnesium iodide is split off from the iodomagnesium-hdyrazobenzene and is thus made available for further reaction. The rate of reaction when smaller proportions of magnesium iodide are used is, however, greatly decreased. Using 50% of magnesium iodide, complete reduction was effected in one week (112% Mg loss); when only 25% of magnesium iodide was employed, two weeks were required for reduction (111% Mg loss).

Reaction of the Reduction Product with Benzoyl Chloride.—The colorless mixture obtained by reducing 7.28 g. of azobenzene was treated with a solution of 11 g. of benzoyl chloride in 20 cc. of benzene. The benzoyl chloride was added in small portions and the mixture was kept cold throughout the reaction. A vigorous reaction ensued and a dark reddish-brown solution resulted. After five hours the mixture was hydrolyzed and it yielded 3.3 g. of dibenzoylhydrazobenzene; m. p. 158°. The product was found to be identical with dibenzoylhydrazobenzene prepared from hydrazobenzene and benzoyl chloride.

The identical results were obtained from iodomagnesium-hydrazobenzene prepared from hydrazobenzene and ethylmagnesium iodide (Equation 4). A solution of ethylmagnesium iodide was prepared from 4.5 cc. of ethyl iodide in a mixture of 30 cc. of ether and 60 cc. of benzene and to the filtered solution solid hydrazobenzene was added in small portions until no further evolution of ethane took place (3.82 g. of hydrazobenzene). This mixture behaved in all respects like the reduction mixture from azobenzene. Addition of 5 cc. of benzoyl chloride gave 1.8 g. of dibenzoylhydrazobenzene.[7]

Reaction with Iodine.—Five grams of iodine was added in portions to the colorless reduction mixture from 3.64 g. of azobenzene. Cooling was necessary because a considerable amount of heat was developed in the reaction. At first the solution became dark-blue in color, then black-brown and finally reddish-brown. After two hours, hydrolysis gave 3.3 g. (90%) of azobenzene, 0.2 g. of hydrazobenzene and 0.1 g. of a black material. The iodomagnesium-hydrazobenzene prepared from hydrazobenzene and a Grignard reagent reacted with iodine in the same manner; the same color changes were observed and azobenzene was obtained in practically the same yield.

Reaction with Oxygen.—When a colorless solution of iodomagnesium-hydrazobenzene is exposed to the air for but an instant, the solution immediately becomes opaque blue-black and then brown-black in color. These colors, like the colors produced during the process of reduction, are due, as explained before, to the formation of quinhydrone-like complexes between the iodomagnesium-hydrazobenzene and azobenzene (the latter compound being furnished here by oxidation).

Dry air was passed into a solution of iodomagnesium-hydrazobenzene for two hours; the following color changes were observed: deep blue, greenish-brown, reddish-brown, dark brown. Hydrolysis gave a 90% yield of azobenzene and no hydrazobenzene. A similar result was obtained when air was passed into iodomagnesium-hydrazobenzene which had been prepared from hydrazobenzene.

Reaction with Carbon Dioxide.—Dry carbon dioxide was passed into the colorless reduction mixture prepared from 7.28 g. of azobenzene; the mixture was kept at 20° throughout the reaction. The grayish-white precipitate which was originally present disappeared completely after one hour and two liquid layers were obtained. After one and one-half hours of carbonation, a mixture of ice and water was added; a large amount of the salt of hydrazobenzene-N,N-dicarboxylic acid (Equation 8) precipitated in the aqueous solution. The benzene–ether solution which was removed was found to contain only 0.72 g. (10%) of product. The aqueous solution was filtered from the solid; the clear filtrate rapidly became cloudy because the salt of the acid loses carbon dioxide and gives hydrazobenzene. When the aqueous solution was acidified, the free acid was precipitated as a solid; it decomposed in a short time into carbon dioxide and hydrazobenzene. Schlenk and Appenrodt observed the same kind of reaction in the case of the sodium addition products of azobenzene.

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[7] Compare Gilman and Pickens, THIS JOURNAL, 47,2406 (1925).

Practically identical results were obtained from iodomagnesium-hydrazobenzene which had been prepared from hydrazobenzene (3.15 g.) and ethylmagnesium iodide. Hydrolysis of the carbonated mixture gave an aqueous solution of the salt of the dicarboxylic acid; acidification of the filtered aqueous solution gave 1.76 g. of hydrazobenzene.

Reaction with **Azoxybenzene.**—Nine and one-tenth grams of azobenzene was reduced and the colorless reduction mixture was treated with 9.9 g. of azoxybenzene in portions; cooling was necessary. The mixture became dark blue, then opaque brown and finally brown-red in color. After twenty hours at room temperature, the solution was hydrolyzed; there was obtained 17 g. of azobenzene and no hydrazobenzene.

Reaction with **Benzil.**—A solution of 10.5 g. of benzil in 30 cc. of benzene was added in the course of five minutes to the iodomagnesium-hydrazobenzene from 9.1 g. of azobenzene. The dark reddish-brown solution which resulted was hydrolyzed after six hours. The solid residue of azobenzene and benzoin which remained after removal of the organic solvents was extracted in a Soxhlet extractor with petroleum ether (40–60°) until the siphoning liquid was colorless. From the extract, 5.6 g. of azobenzene was obtained. The colorless benzoin in the extraction thimble weighed 6.8 g.; by recrystallization from acetic acid it was obtained in the form of colorless needles melting at 132–133°.

Reaction with **Benzaldehyde.**—Addition of 10.6 g. of benzaldehyde in 10 cc. of benzene to the reduction product from 9.1 g. of azobenzene developed a large amount of heat (cooling necessary) and a dark reddish-brown solution resulted. After standing overnight at room temperature, the mixture was hydrolyzed; some aniline and 4.5 g. of benzanilide were obtained. After recrystallization from acetone, the benzanilide melted at 161–162°; the same melting point was observed when the compound was mixed with authentic benzanilide. Benzanilide has been found to be the product when azobenzene is heated at 200° with benzaldehyde.[8]

TABLE I

REDUCTION OF SUBSTITUTED AZOBENZENES BY $Mg + MgI_2$

Compound	G.	Mg *reacted,* %	*Substituted* hydrazobenzene	*Substituted aniline*
4,4′-Dimethylazobenzene	4.20	149	1.80	1.0
4,4′-Dimethoxyazobenzene	4.84	146	....	1.0
4,4′-Diphenylazobenzene	3.34	160	1.08	1.0

In all cases the hydrazobenzene was contaminated with some of the corresponding azobenzene. The reaction with dimethoxyazobenzene is a complex one; the product was a dark oil from which only traces of dimethylhydrazobenzene could be isolated.

In order to obtain some idea concerning the formation of *p*-toluidine (and of aniline from azobenzene), a solution of iodomagnesium-dimethylhydrazobenzene, prepared from dimethylhydrazobenzene (4.2 g.) and the Grignard reagent, was allowed to react with a mixture of magnesium and magnesium iodide. After six days of shaking at room temperature, 0.23 g. (48%) of magnesium had reacted and hydrolysis gave 2.0 g. of a mixture of dimethylhydrazobenzene and dimethylazobenzene and 1.0 g. of p-toluidine. Several formulations for the reaction suggest themselves but the correct one cannot be decided at this time.

Reduction of Azoxybenzene (One Equivalent of Magnesium).—A mixture of 3.96 g. (0.02 mole) of azoxybenzene, 0.486 g. (0.02 atom) of magnesium ribbon and 5.5 g. of magnesium iodide in ether and benzene was shaken until all of the magnesium had disappeared. The reddish-brown solution which contained a small amount of precipitate was hydrolyzed; 3.4 g. of azobenzene and no hydrazobenzene was obtained.

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[8] Bamberger, *Ber.*, 57, 2085 (1924); Bigiavi, *Gazz. chim. ital.*, 57, 160 (1927).

Reduction of Azoxybenzene (Two Equivalents of Magnesium).—To a filtered solution of magnesium iodide, prepared from 6 g. of iodine in 20 cc. of ether and 40 cc. of benzene, was added 4.95 g. of azoxybenzene and a magnesium rod. After three days of shaking the mixture was colorless and contained a precipitate; the mixture had the appearance of the reduction mixture obtained from azobenzene; loss in magnesium, 1.20 g.; calculated, 1.21 g. Hydrolysis gave 4.2 g. (92%) of hydrazobenzene.

The product obtained by the complete reduction of azoxybenzene was identical with the reaction product obtained by reduction of azobenzene. It reacted with azoxybenzene, with iodide and with oxygen, giving azobenzene as the principal product in each case.

TABLE II

REDUCTION OF SUBSTITUTED AZOXYBENZENES BY $Mg + MgI_2$

Compound	G.	Mg reacted, %	Substituted hydrazobenzene	Substituted aniline
4,4′-Dichloroazoxybenzene	5.34	96	4.0	..
4,4′-Dimethoxyazoxybenzene	4.30	110	0.5	..
4,4′Diphenylazoxybenzene	1.75	123	.83	0.35

Reduction of Nitrosobenzene to **Hydrazobenzene.**—To a filtered solution of magnesium iodide, prepared from 36 g. of iodine in a mixture of 40 cc. of ether and 80 cc. of benzene, was added 10.7 g. of nitrosobenzene and a rod of magnesium. The nitrosobenzene dissolved and a reddish-brown solution was obtained; however, after two minutes a complex of nitrosobenzene and magnesium iodide precipitated as an oil which quickly solidified. After ten minutes a large amount of the tan-colored crystals of the complex was present.

During this time reduction had begun and after half an hour the mixture was black in color. This color gradually disappeared and at the end of the reaction the mixture was light brown in color and contained a finely divided solid. The loss in weight of the magnesium rod was 3.76 g.; calculated, 3.65 g. (Equations 11 and 3). Half a dozen similar experiments gave exactly the same loss (103% of the calculated value) of magnesium. Hydrolysis of the mixture gave 6 g. (66%) of hydrazobenzene. Although the amount of magnesium that reacted corresponded closely to that required by Equations 11 and 3, nevertheless the yield of hydrazobenzene was never more than 70% of the calculated amount, which indicates that side reactions occur. The by-products appear to be of the nature of aniline-black. No reduction of nitrosobenzene occurred when it was shaken with magnesium without the addition of magnesium iodide.

When the reaction mixture was treated with iodine or with oxygen, azobenzene was obtained in 65–70% yields.

Reduction of Nitrosobenzene to **Azobenzene.**—A mixture of 5.35 g. of nitrosobenzene, 1.216 g. of magnesium ribbon and 15 g. of magnesium iodide in 20 cc. of ether and 40 cc. of benzene was shaken until all of the magnesium had disappeared. Hydrolysis of the black mixture gave 3.26 g. (71%) of azobenzene and no hydrazobenzene (Equation 11).

It was considered that azoxybenzene might be formed prior to azobenzene. However, when just enough reducing agent was employed to convert all of the nitrosobenzene to azoxybenzene (0.608 g. of magnesium for 5.35 g. of nitrosobenzene), the product consisted of a mixture of unchanged nitrosobenzene and azobenzene (33% yield).

Reaction of the Reduction Mixture with Nitrosobenzene.—To the fully reduced product from 5.35 g. of nitrosobenzene was added 2.68 g. of nitrosobenzene. A vigorous reaction took place with evolution of heat and a dark black mixture resulted. After twenty hours the mixture was hydrolyzed, and gave 4.8 g. (70% of that calculated in Equation 12) of azobenzene.

Summary

Azobenzene is reduced by the system Mg + MgI_2 to iodomagnesium-hydrazobenzene according to the reaction $C_6H_5N{=}NC_6H_5 + Mg + MgI_2 \longrightarrow C_6H_5(MgI)N{-}N(MgI)C_6H_5$.

Azoxybenzene is reduced by the binary system to azobenzene or to the hydrazobenzene derivative according to the amount of reducing agent employed.

Substituted azobenzenes and azoxybenzenes react in the manner of the unsubstituted compounds except that in certain instances reduction proceeds to a considerable extent beyond the hydrazobenzene stage

Nitrosobenzene is reduced principally to iodomagnesium-hydrazobenzene according to the following formulation: $2C_6H_5N{=}O + 3Mg + 3MgI_2 \longrightarrow C_6H_5(MgI)N{-}N(MgI)C_6H_5 + 2(MgI)_2O$. Azobenzene is formed as an intermediate product in this reaction.

The results obtained, in agreement with those of previous studies, lend support to the hypothesis that the active reducing agent is MgX, generated by interaction of magnesium and magnesium halide.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

CONDENSATIONS OF SECONDARY AMINES WITH NAPHTHOLS AND ALDEHYDES. II

BY WALLACE R. BRODE AND JOSEPH B. LITTMAN

RECEIVED JANUARY 10, 1931 PUBLISHED APRIL 6, 1931

In earlier papers by the authors a description has been given, of the preparation[1] of a few condensation products of the type which might be associated with the intermediates formed in the Claisen or Knoevenagel reactions, and the resolution of one of these condensation products *(1-(a-*1-piperidylbenzyl)-2-naphthol),[2] into its optical antipodes. The present paper describes the preparation of several more condensation products involving other aromatic and aliphatic aldehydes. A preparation is also described in which a-naphthol is used in place of 8-naphthol in these condensations.

The mechanism of the a-naphthol condensation was shown to be the same as that of the β-naphthol condensation by the preparation of the α-naphthol derivative through the interaction of benzylidene-dipiperidine and a-naphthol.

The structure of the naphthol derivative (2-(a-1-piperidylbenzyl)-1-

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[1] Littman and Brode, THIS JOURNAL, 52, 1655 (1930).

[2] Brode and Littman, *ibid.*, 52,5056 (1930).

naphthol) was assigned by analogy from similar condensation products which have been previously prepared and analyzed.[3,4,5]

Experimental

The tertiary amines described in this paper were prepared by the following general method: 0.1 mole of naphthol (*a*- or β-) and 0.1 mole of aldehyde were dissolved in 10 cc. of absolute alcohol and to this solution 0.1 to 0.15 mole of secondary amines was added. The solution generally darkened in color and a rise in temperature was noted. On standing from two days to five months the crystalline amine separated out, which was then easily recrystallized from ligroin–alcohol or benzene–alcohol mixtures. The yields varied from 20 to 70% of the theoretical. The hydrochlorides were prepared by passing dry hydrogen chloride gas into a benzene solution of the amine.

TABLE I

PREPARATION, CONSTANTS AND ANALYSES OF AMINES

Amine (-Naphthol)	Naph- thol	Aldehyde	Amine	M. p., °C.	Analyses, % Calcd.	Found
1-(a-Di-n-propylaminobenzyl)-2-	β-	Benz-	Di-n-Pr	95	N, 4.2	4.06
1-(α-Dimethylaminoanisyl)-2-	β-	Anis-	Dimethyl[a]	132	N, 4.56	4.37
1-(α-1-Piperidylanisyl)-2-	β-	Anis-	Piperidine	134.5	Cl, 9.2	9.07
1-(α-Dimethylaminopiperonyl)-2-	β-	Piperonal	Dimethyl"	120	N, 4.36	4.34
2-(α-1-Piperidylbenzyl)-1-	a-	Benz-	Piperidine	110	Cl, 10.0	9.9

[a] An excess of dimethylamine was introduced as a gas.

The tertiary amine, 2-(α-1-piperidylbenzyl)-1-naphthol is very soluble in ether and only slightly soluble in alcohol. The alcohol solution is colored light yellow and on heating the color becomes very intense. On cooling the alcohol solution in a freezing mixture, the color disappears and on warming it reappears. This process may be repeated many times with no apparent effect on the resulting crystalline product or its melting point.

Summary

Several new condensation products formed by the interaction of secondary amines, aromatic aldehydes and β-naphthol have been prepared and described. A description is also given of the application of this type of condensation to secondary amines, aromatic aldehydes and or-naphthol.

COLUMBUS, OHIO

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[3] Betti, *Gazz. chim. ital.*, 31, II, 209 (1901).

[4] Borche and Berkhout, Ann., 330,104 (1904).

[5] Auwers and Dombrowski, *ibid.*, 344, 289 (1906) [indicates condensation in 4 position].

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

THE SYNTHESIS OF ALPHA,BETA-UNSATURATED ETHERS

BY WALTER M. LAUER AND MARVIN A. SPIELMAN

RECEIVED JANUARY 12, 1931 PUBLISHED APRIL 6, 1931

The recent work of Swallen and Boord[1] and Dykstra, Lewis and Boord[2] has drawn attention to the possibilities of halogenated ethers in organic synthesis. The present paper deals with a synthesis of α,β-unsaturated ethers by the use of halogenated ethers in a series of four reactions as shown in the equations

$$RCH_2CHO + R'OH + HCl \longrightarrow RCH_2CH(OR')Cl + H_2O \quad (1)$$
$$RCH_2CH(OR')Cl + Br_2 \longrightarrow RCHBrCH(OR')Br + HCl \quad (2)$$
$$RCHBrCH(OR')Br + R''MgBr \longrightarrow RCHBrCH(OR')R'' + MgBr_2 \quad (3)$$
$$RCHBrCH(OR')R'' + KOH \longrightarrow RCH{=}C(OR')R'' + KCl + H_2O \quad (4)$$

The first three steps in the synthesis were developed by Boord and his co-workers, and in the present work they were carried out in substantially the manner described by these investigators. The last step represents the removal of the elements of hydrobromic acid from a β-bromo ether.

Boord comments on the unusual stability of β-bromo ethers to sodium hydroxide and states that they may be distilled from solid caustic soda without appreciable decomposition. This has been our experience, but we have found finely powdered potassium hydroxide to be an effective reagent for the elimination of hydrobromic acid. In many cases two or three distillations of a β-bromo ether from this substance are sufficient to complete the reaction. Several other reagents were tried, among which were alcoholic potash, quinoline, dimethylaniline, sodium acetate, sodium oxide, potassium carbonate, barium hydroxide, etc. The first two were partially effective, but the yields were small, due to complicating side reactions; the others were almost entirely inert.

It is interesting to note that Hibbert[3] found the same reagent, solid potassium hydroxide, to be the most suitable in the preparation of divinyl ether from β,β'-dichloroethyl ether.

Four vinyl ethers, III, V, VIII and XI, were synthesized as shown below. The α,β-dibromo ethers I, VI and IX given as starting materials were prepared as indicated in equations (1) and (2) above. The proper aldehyde, with an alcohol and gaseous hydrogen chloride, is converted to an a-chloro ether, and this on bromination yields the desired α,β-dibromo ether. By treatment with the Grignard reagent, β-bromo ethers II, IV, VII and X are obtained, and these are distilled from potassium hydroxide to produce the vinyl ethers.

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[1] Swallen and Boord, THIS JOURNAL, 52, 651 (1930).

[2] Dykstra, Lewis and Boord, ibid., 52, 3396 (1930).

[3] Hibbert, Perry and Taylor, ibid., 51, 1551 (1929).

$$\underset{\text{I}}{CH_2BrCH(OC_2H_5)Br} \xrightarrow{C_2H_5MgBr} \underset{\text{II}}{CH_2BrCH(OC_2H_5)C_2H_5} \xrightarrow{KOH} \underset{\text{III}}{CH_2{=}C(OC_2H_5)C_2H_5}$$

$$\xrightarrow{C_6H_5MgBr} \underset{\text{IV}}{CH_2BrCH(OC_2H_5)C_6H_5} \xrightarrow{KOH} \underset{\text{V}}{CH_2{=}C(OC_2H_5)C_6H_5}$$

$$\underset{\text{VI}}{CH_3CHBrCH(OCH_3)Br} \xrightarrow{C_6H_5MgBr} \underset{\text{VII}}{CH_3CHBrCH(OCH_3)C_6H_5} \xrightarrow{KOH} \underset{\text{VIII}}{CH_3CH{=}C(OCH_3)C_6H_5}$$

$$\underset{\text{IX}}{C_2H_5CHBrCH(OCH_3)Br} \xrightarrow{C_2H_5MgBr} \underset{\text{X}}{C_2H_5CHBrCH(OCH_3)C_2H_5} \xrightarrow{KOH} \underset{\text{XI}}{C_2H_5CH{=}C(OCH_3)C_2H_5}$$

The substituted vinyl ethers are ethereal liquids, miscible with the usual organic solvents and easily distilled without decomposition. In the presence of a trace of acid, or even semicarbazide hydrochloride, they hydrolyze to the corresponding ketones.

$$RCH{=}C(OR')R'' + H_2O \longrightarrow RCH_2COR'' + R'OH$$

This property was used as a constitution proof for those not described in the literature. The ketones were characterized as semicarbazones.

Experimental Part

A. Preparation of the Chloro Ethers. Equation (I).—The procedure followed was essentially that described by Boord. In working with propionaldehyde or butyraldehyde, however, greater care was necessary. When the aldehyde and alcohol were mixed, considerable heat was evolved, and if thorough cooling with an ice–salt bath was not effected before the influx of the hydrogen chloride, unmanageable colored liquids were obtained from which none of the desired product could be isolated.

B. Preparation of the α,β-Dibromo Ethers. Equation (2).—The α-chloro ethers were brominated without purification and without a solvent in an ice–salt bath at 0–5°. Bromine was added in small portions as fast as it was taken up. After the last had been added, the mixture was allowed to stand overnight and then distilled under diminished pressure. The average yields based on the aldehyde taken for the first reaction were about 70%.

C. Preparation of the β-Bromo Ethers. Equation (3).—The Grignard reactions were carried out by the improved procedure described by Boord in his second paper.[3]

β-Ethoxybutyl Bromide (II).—Yield, 80%; n^{25}_D 1.4427; b. p. 154–156° (Boord reports 166°).

α-Phenyl-β-bromoethyl Ethyl Ether (IV).—Yield, 66%; b. p. 129–133° at 18 mm.; n^{25}_D 1.5317.

Anal. Calcd. for $C_{10}H_{13}OBr$: Br, 34.93. Found: Br, 35.38, 35.51.

α-Phenyl-β-bromopropyl Methyl Ether (VII).—Yield, 71%; b. p. 122–124° at 14 mm.; n^{25}_D 1.5316. This compound has been synthesized by Spath and Göhring[4] by the same Grignard reaction. The violet color observed by these workers was apparent for a time, but soon faded out.

3-Bromo-4-methoxy-hexane (X).—Yield, 56%; b. p. 74–78' at 20 mm.; n^{25}_D 1.4495.

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[4] Spath and Gohring, *Monatsh.*, 41, 319 (1920).

Anal. Calcd. for $C_7H_{15}OBr$: Br, 41.03. Found: Br, 40.23, 40.20.

D. Preparation of the **α,β-Unsaturated** Ethers, Equation (4).—In a distilling flask connected to a condenser was placed 40–60 g. of the β-bromo ether with an equal weight of finely powdered technical grade flake potassium hydroxide. A large sand-bath was placed under the flask and the temperature was raised very slowly to incipient boiling and maintained at that level for half an hour or longer. More heat was then applied and distillation was allowed to take place over a period of two hours. Suction was advantageously employed in distilling off the last of the material from the potash, which generally fused toward the end of the reaction. In the case of compounds (V) and (VXII) most of the distillation was conducted under diminished pressure to delay the fusion of the alkali and subsequent "layering out" of materials. In three of the four compounds studied, three such distillations were sufficient to remove the last of the bromine, as indicated by the Beilstein test. The products were then purified by distillation.

2-Ethoxy-butene-1 (III).—Yield, 65%; some unchanged halide was recovered, bringing the yield up to 75.6%; b. p. 85–87'; $n_D^{24.5}$ 1.4011.

And. Calcd. for $C_6H_{12}O$: OC_2H_5, 45.0. Found: OC_2H_5, 44.9, 44.4.

One-half cc. was hydrolyzed with 5 cc. of water, 0.5 g. of semicarbazide hydrochloride and enough alcohol to effect solution. The hydrolysis proceeded spontaneously. Sodium acetate was added and after half an hour of heating in a beaker of water the test-tube was cooled and the methyl ethyl ketone semicarbazone separated out. After crystallization from hot water it melted at 143–144.5". Pickard and Kenyon[5] give 135–136°, Robinson' gives 148° and Michael[7] gives 139°. A sample prepared from authentic methyl ethyl ketone melted at 143–144° and a mixed melting point showed no depression.

a-Ethoxystyrene (V).—Yield, 62%; b. p. 109–112° at 30 mm.; $n_D^{25.5}$ 1.5287. This compound has been prepared by Hoering,[8] Claisen,[9] Moureu,[10] and Tiffeneau.[11] It was hydrolyzed to acetophenone, which was identified as the semicarbazone; m. p. and mixed m. p. 198–199°. Shriner[12] gives the same figure.

a-Methoxy-p-methylstyrene (VIII).—Yield, 42%; b. p. 96–98° at 19 mm.; n_D^{26} 1.5271.

Anal. Calcd. for $C_9H_{12}O$: OCH_3, 20.9. Found: OCH_3, 20.9, 21.3.

This compound was collected by Spath and Göhring[4] as a by-product in their synthesis of ephedrine, but not in a form sufficiently pure for analysis. One cc. was hydrolyzed by warming with 50% alcohol and a drop of hydrochloric acid. The propiophenone which settled out on dilution was converted to the semicarbazone: m. p. and mixed m. p. 172–174". Shriner[12] gives 173–174°.

3-Methoxyhexene-3 (XI).—Yield, 79%; b. p. 114–115°; n_D^{25} 1.4130.

Anal. Calcd. for $C_7H_{14}O$: OCH_3, 27.2. Found: OCH_3, 27.3, 27.7.

This was hydrolyzed to ethyl propyl ketone and converted to the semicarbazone: m. p. 110–110.5". Michael[7] gives 111°. Blaise[13] gives 110°.

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[5] Pickard and Kenyon, J. *Chem. Soc.*, 103,1936 (1913).

[6] Robinson, *ibid.*, 109,1044 (1916).

[7] Michael, THIS JOURNAL, 41,416 (1919).

[8] Hoering, *Ber.*, 41, 1889 (1908).

[9] Claisen, *ibid.*, 29,2931 (1896); 31, 1020 (1898).

[10] Moureu, ***Bull. soc. chim.***, [3] 31,493 (1904).

[11] Tiffeneau, *Compt. rend.*, 145, 813 (1907).

[12] Shriner and Turner, THIS JOURNAL, 52, 1269 (1930).

[13] Blaise, *Compt. rend.*, 133,1218 (1901).

Summary

A method for the synthesis of α,β-unsaturated ethers is described and examples are given. This method appears to be quite general in its application.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION PROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

MIXED BENZOINS.
III. THE STRUCTURE OF SOME UNSYMMETRICALLY SUBSTITUTED DESOXYBENZOINS

BY JOHANNES S. BUCK AND WALTER S. IDE

RECEIVED JANUARY 22, 1931 PUBLISHED APRIL 6, 1931

In general, the structure of a mixed benzoin, when produced in the usual manner from two aldehydes, cannot be assigned with any degree of probability. The same remark applies to the desoxy compound derived from it by the usual methods of reduction, for even were the structure of the mixed benzoin known, the desoxy compound might be derived from it via the hydrobenzoin or the isohydrobenzoin, from which compounds water can be eliminated in several ways. Thus RCOCHOHR' could give RCHOH-CHOHR' which, by elimination of a molecule of water, could give either $RCOCH_2R'$ or RCH_2COR' by the "vinyl-dehydration" of Tiffeneau. Other compounds, for example, diphenylacetaldehydes, produced by the "pinacoline-dehydration" of Tiffeneau, might also be expected to occur. The authors therefore sought for an unambiguous reaction to prove the structure of desoxy compounds and selected for this purpose the Beckmann transformation. A given mixed benzoin, on reduction, can give two desoxy compounds, each of which can, in turn, give two oximes. With a suitable reagent these oximes are converted into amides, the amide being different in each case. The amides are readily identified, either by hydrolysis or by synthesis, so that it is possible to assign a structure to both the oxime and to the parent desoxy compound. Usually a mixed benzoin gives but one desoxy compound, but this is not general.[1] In turn a given desoxy compound yields usually only one oxime, but again this is not general, the authors having in one case obtained both oximes in sufficient amounts to carry out Beckmann transformations on them.

There appears to be only one instance recorded of the application of the Beckmann transformation to a desoxy type of compound,[2] in this case produced by a Friedel-Crafts reaction and of known structure. The present authors have applied the transformation to seven desoxy compounds

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[1] Jenkins, Buck and Bigelow, THIS JOURNAL, 52, 4495 (1930).

[2] Cain, Simonsen and Smith, *J. Chem. Soc.*, 103, 1035 (1913).

which were produced by the direct reduction of mixed benzoins, and have established the structure of these and of their oximes. The choice of the benzoins used was purely a matter of expediency, the most readily accessible ones being selected. The case of desoxydimethylaminobenzoin[1] was included in order to check the somewhat involved reasoning used in deducing its structure.

In a later paper it is hoped, after certain difficulties have been overcome, to apply the Beckmann transformation to the mixed benzoins themselves, since their structure cannot with certainty be inferred from the structure of the desoxy compounds.

Desoxy compounds of the mixed benzoins formed from the following pairs of aldehydes were investigated: (1) o-chlorobenzaldehyde and veratric aldehyde,[4] (2) o-chlorobenzaldehyde and anisaldehyde,[4] (3) *o*-chlorobenzaldehyde and *p*-dimethylaminobenzaldehyde,[3] (4) *o*-chlorobenzaldehyde and piperonal,[3] (5) benzaldehyde and anisaldehyde,[5] (6) benzaldehyde and piperonal,[3] and (7) benzaldehyde and *p*-dimethylaminobenzaldehyde.[1]

The desoxybenzoin from benzoin (1) gave 1-chlorophenylacet-3,4-dimethoxyanilide, and is hence 1-chlorobenzyl-3,4-dimethoxyphenyl ketone. Its oxime is the syn-dimethoxyphenyl derivative. The desoxy compound from benzoin *(2)* gave similarly 1-chlorophenylacetanisidide, showing that it is 1-chlorobenzyl-4-methoxyphenyl ketone and its oxime the syn-methoxyphenyl compound. From the desoxy compound of benzoin (3) 1-chlorophenylacet-4-dimethylaminoanilide was obtained and hence the desoxy compound is 1-chlorobenzyl-4-dimethylaminophenyl ketone and its oxime is the syn-dimethylaminophenyl oxime. The desoxy compound from benzoin (4) has an analogous structure, 1-chlorophenylacet-3,4-methylenedioxyanilide being formed on transformation of the oxime. The desoxy compound is therefore 1-chlorobenzyl-3,4-methylenedioxyphenyl ketone and the oxime is the syn-methylenedioxyphenyl compound.

From the desoxy compound of benzoin (5) two oximes were obtained. The syn-phenyl oxime gave 4-methoxyphenylacetanilide, while the *anti*-phenyl oxime gave benzoyl-4-methoxybenzylamine. Both these products indicate that the desoxybenzoin is 4-methoxybenzyl phenyl ketone. Tiffeneau and OrCkhoff[6] have described a compound, prepared in a different manner, to which they assign the same structure. Their compound appears to be identical with that of the present authors. As a check of the

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[3] Buck and Ide, THIS JOURNAL, 52,220 (1930).

[4] Buck and Ide, *ibid.*, 52,4107 (1930).

[5] Previously obtained by several workers. The preparation used was that of Kinney, *ibid.*, 51,1592 (1929).

[6] Tiffeneau and Orékhoff, *Bull. soc. chim.*, [4] 37,430, 1410 (1925).

method, benzyl-4-methoxyphenyl ketone was prepared by a Friedel–Craft reaction. From it only one oxime was obtained, and this was transformed into phenylacetanisidide, showing that the oxime had the *syn*-methoxyphenyl structure and confirming the method. As a further check, the last possible isomeric amide, 4-methoxybenzoylbenzylamine was prepared and found to differ from the other three amides obtained in the transformations. This series is shown in full below, to illustrate the reactions and the principles involved in this work.

Tiffeneau and Lévy[7] describe phenyl-3,4-methylenedioxybenzyl ketone, obtained by distilling the oxide of α-phenyl-β-3,4-methylenedioxyethylene. They give the melting point as 71–72°. The desoxy compound obtained by the present authors melts at 86° and its oxime, by the Beckmann transformation, gives phenylacet-3,4-methylenedioxyanilide, showing that the oxime is the anti-benzyl compound and that the desoxy compound is the isomer of Tiffeneau and Lévy's ketone and is benzyl-3,4-methylenedioxyphenyl ketone.

The structure of β-desoxy-*p*-dimethylaminobenzoin was earlier deduced by rather involved reasoning[2,8] and it was desirable to check this. The oxime gave phenylacet-4-dimethylaminoanilide and hence the β-desoxy compound is benzyl-4-dimethylaminophenyl ketone, as previously stated, and the oxime is the anti-benzyl oxime.

The yields of the desoxy compounds are frequently mediocre. It is quite possible that the isomeric desoxy compound and the diphenylacetaldehyde were present in some cases, but no serious attempt to isolate these was made, for the present purpose.

A few of the amides encountered hydrolyzed under rather drastic treatment. The acid fragment was readily isolated, but the basic fragment was degraded by the reagent used. This is to be expected with amines such as dimethyl-*p*-phenylenediamine.[9] For this reason the structure of the amide was checked synthetically in all cases. For practical purposes the identification of the acid fragment is sufficient. The majority of the amides resisted hydrolysis even by powerful reagents.

The authors have avoided assigning definite names to the mixed benzoins (*cf.* Buck and Ide[3]) on account of the ambiguity in their structure. It is hoped to clear up this point soon.

The structures of the desoxy compounds and of their oximes have been deduced on the assumption that the transformation takes place directly, between the vicinal groups of the oximes, and that no transposition of groups, such as that suggested by Meisenheimer[10] for the benzil oximes,

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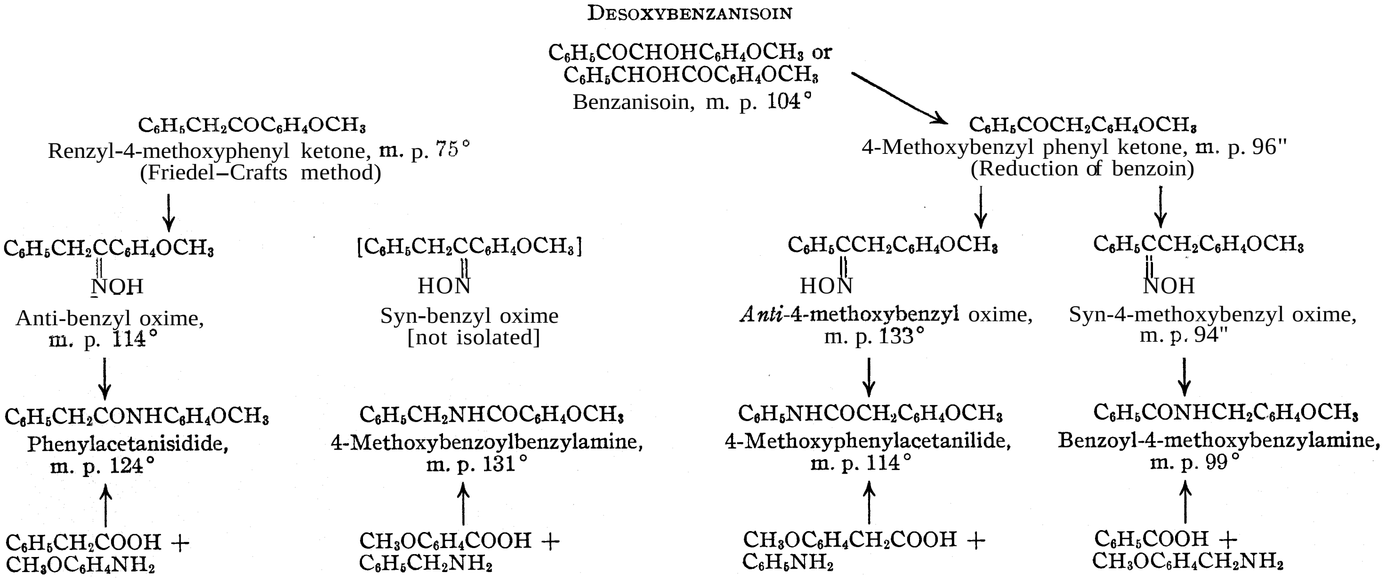
[7] Tiffeneau and Lévy, *Compt. rend.*, 190, 1510 (1930).

[8] Jenkins, Bigelow and Buck, THIS JOURNAL, 52, 5198 (1930).

[9] Cf. Merz, Weith and Weber, *Ber.*, 10, 762 (1877).

[10] Meisenheimer, *ibid.*, 54, 3206 (1921).



DESOXYBENZANISOIN

$C_6H_5COCHOHC_6H_4OCH_3$ or $C_6H_5CHOHCOC_6H_4OCH_3$
Benzanisoin, m. p. 104°

$C_6H_5CH_2COC_6H_4OCH_3$
Renzyl-4-methoxyphenyl ketone, m. p. 75°
(Friedel–Crafts method)

$C_6H_5COCH_2C_6H_4OCH_3$
4-Methoxybenzyl phenyl ketone, m. p. 96"
(Reduction of benzoin)

$C_6H_5CH_2\underset{\underset{NOH}{\|}}{C}C_6H_4OCH_3$
Anti-benzyl oxime, m. p. 114°

$[C_6H_5CH_2\underset{\underset{HON}{\|}}{C}C_6H_4OCH_3]$
Syn-benzyl oxime [not isolated]

$C_6H_5\underset{\underset{HON}{\|}}{C}CH_2C_6H_4OCH_3$
Anti-4-methoxybenzyl oxime, m. p. 133°

$C_6H_5\underset{\underset{NOH}{\|}}{C}CH_2C_6H_4OCH_3$
Syn-4-methoxybenzyl oxime, m. p. 94"

$C_6H_5CH_2CONHC_6H_4OCH_3$
Phenylacetanisidide, m. p. 124°

$C_6H_5CH_2NHCOC_6H_4OCH_3$
4-Methoxybenzoylbenzylamine, m. p. 131°

$C_6H_5NHCOCH_2C_6H_4OCH_3$
4-Methoxyphenylacetanilide, m. p. 114°

$C_6H_5CONHCH_2C_6H_4OCH_3$
Benzoyl-4-methoxybenzylamine, m. p. 99°

$C_6H_5CH_2COOH + CH_3OC_6H_4NH_2$

$CH_3OC_6H_4COOH + C_6H_5CH_2NH_2$

$CH_3OC_6H_4CH_2COOH + C_6H_5NH_2$

$C_6H_5COOH + CH_3OC_6H_4CH_2NH_2$

takes place. The amides actually obtained could not have been produced had a transposition of groups occurred. Further strong evidence in favor of the authors' assumption, is afforded by the fact that the oximes of several desoxy compounds whose structures have been established by other methods (v. s.) gave without exception the amides to be expected on the basis of a straight transformation between the vicinal groups.

TABLE I

KETONES

No.	Phenyl ketones	Formula	From benzoin	Yield, %
(A)[4]	1-Chlorobenzyl-3,4-dimethoxy-	$ClC_6H_4CH_2COC_6H_3(OMe)_2$	(1)	..
(B)[4]	1-Chlorobenzyl-4-methoxy-	$ClC_6H_4CH_2COC_6H_4OMe$	(2)	..
(C)	1-Chlorobenzyl-4-dimethylamino-	$ClC_6H_4CH_2COC_6H_4NMe_2$	(3)	44
(D)	1-Chlorobenzyl-3,4-methylenedioxy-	$ClC_6H_4CH_2COC_6H_3O_2CH_2$	(4)	96
(E)[6]	4-Methoxybenzyl	$MeOC_6H_4CH_2COC_6H_5$	(5)	87
(F)	Benzyl-4-methoxy-	$C_6H_5CH_2COC_6H_4OMe$	...	..
(G)	Benzyl-3,4-methylenedioxy-	$C_6H_5CH_2COC_6H_3O_2CH_2$	(6)	64
(H)[1]	Benzyl-4-dimethylamino-	$C_6H_5CH_2COC_6H_4NMe_2$	(7)	..

The ketones (with the exception of F) were prepared by reducing the benzoin by boiling with tin and concd. hydrochloric acid, in alcoholic solution, for six or more hours (Buck and Ide, Refs. 3 and 4). Ketone F was prepared by a Friedel–Crafts reaction on phenylacetyl chloride and anisole. Ketones A, B, E and H have been described elsewhere, A and B without structures assigned. Ketone E is reduced catalytically to a compound melting at 128.5°, probably the same as Tiffeneau and Orékhoff's compound of m. p. 134–135°.[6] By analogy, it is the hydrobenzoin. It forms silky, white leaves, giving an intense golden-brown color with concd. sulfuric acid (cf. (6) where the color is given as red). Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.73; H, 6.61. Found: C, 73.86; H, 6.77.

No.	M. p., °C.	Appearance	Analyses, % Calcd. C	H	N	Found C	H	N
(C)	122	White needles	70.17	5.88	5.11	70.28	5.87	5.00
(D)	105	White cubes	65.55	4.03		65.87	4.06	
(F)	73	Pearly tables	79.60	6.24		79.58	6.31	
(G)	86	White prisms	74.96	5.37		74.70	5.42	

TABLE II

OXIMES

No.	Phenyl ketoximes	Formula	From ketone
(A)	*Anti*-1-chlorobenzyl-3,4-dimethoxy-	$ClC_6H_4CH_2C({=}NOH)C_6H_3(OMe)_2$	A
(B)	*Anti*-1-chlorobenzyl-4-methoxy-	$ClC_6H_4CH_2C({=}NOH)C_6H_4OMe$	B
(C)	Anti-1-chlorobenzyl-4-dimethylamino-	$ClC_6H_4CH_2C({=}NOH)C_6H_4NMe_2$	C
(D)	*Anti*-1-chlorobenzyl-3,4-methylenedioxy-	$ClC_6H_4CH_2C({=}NOH)C_6H_3O_2CH_2$	D
(E-1)	Anti-4-methoxybenzyl	$MeOC_6H_4CH_2C({=}NOH)C_6H_5$	E
(E-2)	Syn-4-methoxybenzyl	$MeOC_6H_4CH_2(HON{=})CC_6H_5$	E
(F)	Anti-benzyl-4-methoxy-	$C_6H_5CH_2C({=}NOH)C_6H_4OMe$	F
(G)	*Anti*-benzyl-3,4-methylenedioxy-	$C_6H_5CH_2C({=}NOH)C_6H_3O_2CH_2$	G
(H)	Anti-benzyl-4-dimethylamino-	$C_6H_5CH_2C({=}NOH)C_6H_4NMe_2$	H

TABLE II (*Concluded*)

Two methods were used for preparing the oximes. [1] The ketone, in alcoholic solution, was allowed to stand with an excess of hydroxylamine acetate (from the hydrochloride and potassium acetate) and finally warmed for two hours and the mixture then diluted with water. [2] The ketone, in pyridine solution, was warmed on the bath for three hours with hydroxylamine hydrochloride (excess) and the mixture then diluted with water. In either case the product was recrystallized from alcohol until pure.

Oxime E-1 has been described by Tiffeneau and Orékhoff,[6] form undetermined.

Oxime H has been described by Jenkins, Buck and Bigelow,[1] form undetermined.

No.	Yield, %	M. p., °C.	Appearance	Preparation	Nitrogen analyses, % Calcd.	Found
(A)	64	137	Glittering prisms	[1]	4.58	4.78
(B)	86	97	Dull crystals	[1] [2]	5.07	5.07
(C)	61	173	Glittering prisms	[1]	9.70	9 83
(D)	42	120	Glittering rhombs	[1]	4.83	4.72
(E-1)	23	133	....	[1]	..	..
(E-2)	19	94	Felted needles	[1]	5.80	5.97
(F)	94	114	Glittering crystals	[2]	5.80	5.84
(G)	60	103	Tiny needles	[2]	5.48	5.61

Oxime G was accompanied by very small amounts of a second oxime, which formed thick, white prisms, melting at 130°. Anal. Calcd. for $C_{15}H_{13}O_3N$: N, 5.48. Found: N, 5.45.

TABLE III

AMIDES

No.	Name	Formula	From oxime
(A)	1-Chlorophenylacet-3,4-dimethoxyanilide	$ClC_6H_4CH_2CONHC_6H_3(OMe)_2$	A
(B)	1-Chlorophenylacetanisidide	$ClC_6H_4CH_2CONHC_6H_4OMe$	B
(C)	1-Chlorophenylacet-4-dimethylaminoanilide	$ClC_6H_4CH_2CONHC_6H_4NMe_2$	C
(D)	1-Chlorophenylacet-3,4-methylenedioxyanilide	$ClC_6H_4CH_2CONHC_6H_3O_2CH_2$	D
(E-1)	4-Methoxyphenylacetanilide	$MeOC_6H_4CH_2CONHC_6H_5$	E-1
(E-2)	Benzoyl-4-methoxybenzylamine	$C_6H_5CONHCH_2C_6H_4OMe$	E-2
(F)	Phenylacetanisidide	$C_6H_5CH_2CONHC_6H_4OMe$	F
(G)	Phenylacet-3,4-methylenedioxyanilide	$C_6H_5CH_2CONHC_6H_3O_2CH_2$	G
(H)	Phenylacet-4-dimethylaminoanilide	$C_6H_5CH_2CONHC_6H_4NMe_2$	H
(I)	4-Methoxybenzoylbenzylamine	$C_6H_5CH_2NHCOC_6H_4OMe$	...

The amides were synthesized by one of the following two methods, the one used being determined by circumstances: (1) the Schotten–Baumann reaction, (2) heating the acid and amine together in molecular proportions, at 180–200° for two hours.

The Beckmann reaction was carried out in one or both of two ways, (1) by means of benzenesulfone chloride and sodium hydroxide solution, after the manner of a Schotten–Baumann reaction, and (2) by the action of phosphorus pentachloride on the oxime in absolute ether. The first method is convenient, rapid and gives good yields.

Amides A, C and D were hydrolyzed by strong acids, giving o-chlorophenylacetic acid.

TABLE III (*Concluded*)

No.	Synth. prep.	Beck-mann	M. p., °C.	Appearance	Nitrogen analyses, % Calcd.	Found	Refs
(A)	2	2	177	White, slender needles	4.58	4.68	11,12
(B)	2	1	163	Glittering needles	5.07	5.23	
(C)	1	2	165	White prisms	9.70	9.88	
(D)	1	1, 2	175	Dull, white needles	4.83	4.98	13
(E-1)	2	2	113	Buff, slender prisms	5.80	5.72	
(E-2)	1	1	96	Faint yellow plates	5.80	5.89	14
(F)	2	1	121	Glittering crystals	5.80	5.89	
(G)	1	1	146	Buff, pearly plates	5.48	5.65	
(H)	1	1	144	Cream, slender prisms	11.02	10.97	
(I)	2	..	131	White, flaky crystals	5.80	5.98	15

The solubilities of the compounds described are not distinctive. The amides are moderately soluble in alcohol, and rather soluble in benzene, chloroform, etc. The oximes are frequently very soluble in absolute alcohol, but separate readily on the addition of a little water. In every instance the compounds were recrystallized from alcohol until pure. The melting points given are corrected. The identification of the amides obtained in the Beckmann reaction was always carried out by comparison and mixed melting point determinations with a synthetic specimen. The analyses are all microanalyses (Pregl).

Summary

The Beckmann transformation has been used to determine the structures of certain unsymmetrically substituted desoxybenzoins, and to assign configurations to the oximes derived from them. Seven desoxy compounds were examined. **A** number of new desoxy compounds, oximes and amides are described. The results support the view that the transformation takes place between the vicinal groups of the oximes.

TUCKAHOE, NEW YORK

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[11] Preparation of Mehner, *J. prakt. Chem.*, **[2] 62,556 (1900).** [12] 4-Aminoveratrole is conveniently prepared by a method analogous to that of Rupe and Majewski,[13] from veratric oxime, via veratronitrile and veratric amide, upon which a Hofmann reaction is carried out, using the theoretical amount of sodium hypochlorite. [13] Aminopiperole is best prepared by the method of Rupe and Majewski, ***Ber.*, 33,3401 (1900).** The preparation is much improved by using the theoretical amount of sodium hypochlorite in the last stage. Special treatment of the amide is then not necessary. [14] 4-Methoxybenzylamine is readily prepared by the method of Goldschmidt and Polonowska, ***Ber.*. 20,2407 (1887).** [15] Obtained by Beckmann [***Ber.*,37,4138** (1904)] by the action of benzenesulfone chloride on N-benzylanisaldoxime, and also mentioned by Rugheimer, ***Ber.*** 49, **592 (1916).**

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

REACTIONS OF SOME ORGANIC LEAD COMPOUNDS[1]

BY CHARLES D. HURD AND PAUL R. AUSTIN

RECEIVED JANUARY 22, 1931 PUBLISHED APRIL 6, 1931

Many cases exist to show that in the reaction of mineral acids with aryl-alkyl-metal compounds, the aryl group is more readily severed than the alkyl group. Such, for example, is the case with diphenyldiethyllead,[2] triphenylalkyllead[3] (where alkyl represents methyl, ethyl or cyclohexyl), phenylmethylmercury,[4] triphenylbenzyltin[5] and others. On the basis of such evidence, arguments have been advanced that the preferential removal of aryl signifies that aryl groups possess a greater electron attraction than alkyl groups. Although electron attraction is probably the determining factor in compounds like ArHgR or Ar_2PbR_2, with such a compound as Ar_3PbR it might be said that the greater supply of Ar groups is the determining factor. In fact, Calingaert[6] has stated: "It is also worth mentioning that, in (lead) compounds containing different organic radicals, the halogen exerts a very decided selective action, reacting almost invariably with one of the groups of which there is the larger number."

Phenyltriethyllead, therefore, presents an interesting case. With the preponderance of ethyl groups, it might be expected that ethyl, rather than phenyl, should be removed first. With electron attraction as the determining factor the reverse might be expected. Actually, it has been found that hydrochloric acid reacts to cause preferential scission of phenyl to yield benzene and triethyllead chloride. Benzene was identified as *m*-dinitrobenzene. With nitric acid and phenyltriethyllead, the reaction product is diethyllead dinitrate, $Et_2Pb(NO_3)_2$. This dinitrate, hitherto unprepared, was also made by the action of nitric acid on tetraethyllead.

These reactions are best carried out in the presence of chloroform. When undiluted, they are difficult to control. Diethyllead dinitrate is a water-soluble salt which was found to be about 79% ionized in tenth molar solution. Conditions were determined for preparing triethyllead nitrate from tetraethyllead. This nitrate rapidly reacts further to yield the dinitrate. Further interaction apparently yields lead nitrate rather than such a substance as ethyllead trinitrate.

Pyrolysis of Lead Compounds.—It is known that in the pyrolysis of

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[1] This investigation was made possible by the help of Mr. Thomas Midgley, Jr., and Mr. E. W. Webb of the Ethyl Gasoline Corporation, which is gratefully acknowledged. Original manuscript received July 30, 1930.

[2] Moeller and Pfeiffer, *Ber.*, 49, 2441 (1916).

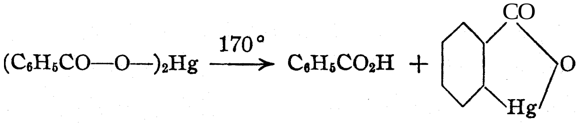
[3] Krause and Schlottig, ibid., 58, 427 (1925).

[4] Kharasch and Marker, THIS JOURNAL, 48, 3139 (1926).

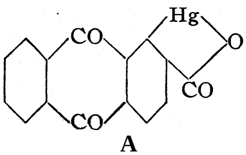
[5] Bullard, *ibid.*, 51, 3065 (1929).

[6] Calingaert, *Chem. Reviews*, **2**, 52 (1925).

mercuric benzoate,[7] benzoic acid is eliminated and a carbon-to-mercury union is established



Mercuric 1,2-anthraquinonedicarboxylate[8] has been found to behave similarly, giving the anhydro hydroxymercuri compound, A, when heated at 235°. Since a C—Hg linkage was established in these reactions, it was of interest to see if a carbon-to-lead linkage could be established by an analogous process, namely, by the pyrolysis of lead tetrabenzoate. We prepared the latter by interaction of lead tetraacetate and benzoic acid, a reaction which has recently been described by Criegee.[9]



A

The pyrolysis of lead tetrabenzoate was always accompanied by a mild explosion, Possibly this could have been avoided by the use of an inert medium, but this was not tried. Although benzoic acid was detached it is not exactly clear how this occurs for no evidence was found for tetravalent lead in the residue. This residue was completely soluble in dilute sodium hydroxide solution and no lead dioxide was formed thereby. Lead dibenzoate was the only lead compound identified. Had such a compound as $\left(C_6H_4\overset{CO_2}{\diagup\!\!\!\diagdown}\right)_2Pb$ been found, (1) the action of bromine on the residue should have yielded o-bromobenzoic acid, but no positive evidence for this could be obtained; (2) sodium hydroxide solution should have yielded ortho $(HO)_2Pb(C_6H_4CO_2Na)_2$ which would have behaved quite differently from the Pb^{++} ions actually found.

Lead acetate and acetic acid, but no other compounds, were noted when lead tetraacetate was decomposed at 190°.

Experimental Part

Triethyllead chloride was prepared from tetraethyllead[10] and concd. hydrochloric acid by the method of Browne and Reid.[11] It, in turn, was added in portions to an ether solution of phenylmagnesium bromide. Phenyltriethyllead was thus prepared by the method of Griittner and Grüttner.[12] They recorded its boiling point as 136° at 13 mm.

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[7] Dimroth, *Ber.*, 35,2870 (1902).

[8] Whitmore and Carnahan, THIS JOURNAL, **51,** 856 (1929).

[9] Criegee, *Ann.*, 481,284 (1930).

[10] A generous supply of this material was donated by the Ethyl Gasoline Corporation.

[11] Browne and Reid, THIS JOURNAL, 49, 836 (1927). Gilman and Robinson, *ibid.*, 52, 1975 (1930) describe a preparation using tetraethyllead, ether and hydrogen chloride.

[12] Griittner and Griittner, *Ber.*, 51, 1296 (1918).

Tetraethyllead and Nitric Acid.—One hundred grams of tetraethyllead and 350 cc. of chloroform were placed in a 3-necked flask and 28 cc. of concd. nitric acid was added drop by drop into the boiling solution. Then it was refluxed for one and one-half hours. At the start of the reflux period a heavy liquid layer, presumably a mixture of triethyl- and diethyllead nitrates, appeared. This gradually became solid as the reaction progressed. The solid was filtered while hot. About 50 g. of impure diethyllead dinitrate was collected on the filter. It was identified by conversion into diethyllead dichloride by dissolving it in methanol and adding concd. hydrochloric acid. The mixture was filtered from lead chloride and the filtrate concentrated. The diethyllead dichloride which precipitated was washed with ether, dried and analyzed.

Anal. Calcd. for $(C_2H_5)_2PbCl_2$: Pb, 61.5; Cl, 21.1. Found: Pb, 61.3; Cl, 20.8.

The filtrate, on cooling, gave a small precipitation of a salt analyzing 60–61% of lead which was evidently triethyllead nitrate for the most part. The calcd. Pb in $(C_2H_5)_3PbNO_3$ is 58.1%, and in $(C_2H_5)_2Pb(NO_3)_2$ is 53.2%. Some lead nitrate was also in it. The same substance was found to precipitate at the beginning of the reaction if it was chilled.

Phenyltriethyllead and Nitric Acid.—Three cc. of nitric acid was added to a solution of 8 g. of phenyltriethyllead in 100 cc. of chloroform. A liquid layer formed. The solution was refluxed for fifteen minutes, filtered hot and the filtrate cooled. The 1.3 g. of crystalline diethyllead dinitrate which appeared was collected. Another 0.9 g. was obtained by extracting the residue from the first filtration. These crystals were soluble in water and the solution gave no test for lead ion with potassium dichromate solution.

Anal. Calcd. for $(C_2H_5)_2Pb(NO_3)_2$: Pb, 53.2. Calcd. for $(C_6H_5)(C_2H_5)Pb(NO_3)_2$: Pb, 47.3. Found: Pb, 53.1, 52.9.

Fractionation of the chloroform solution gave a fraction which contained benzene. Thus, nitration of this fraction yielded m-dinitrobenzene which melted at 88°. A mixed melting point determination with an authentic specimen of m. p. 90°, was 89°.

Conversion of the dinitrate into the dichloride was effected in the manner previously described with the dinitrate from tetraethyllead.

Reaction without Diluents.—Small yields of diethyllead dinitrate which analyzed 53.0% of lead were obtained when 0.9 cc. of nitric acid (sp. gr. 1.4) was dropped onto 2 g. of phenyltriethyllead at room temperature. Far better yields were obtained when solvents were employed, and of these chloroform appeared to give better results than benzene or ether.

Dissociation of Diethyllead Dinitrate.—The apparent molecular weight of this salt was determined by the freezing point method, using water as the solvent. In two experiments, these findings were 150.9 and 150.0, whereas the true molecular weight of $(C_2H_5)_2Pb(NO_3)_2$ is 389.

Data. Subs., 0.8085, 0.4581: H_2O, 20 and 20 g.; moles of the salt per 1000 g. of H_2O, 0.104, 0.059; depression of the freezing point, 0.498°, 0.284°.

From these data, calculation of the percentage ionization of diethyllead dinitrate into three ions gave values of 78.8 and 79.5%, respectively.

Phenyltriethyllead and Hydrochloric Acid.—One hundred cc. of chloroform and 12.7 g. of phenyltriethyllead (b. p. (10 mm.) 128–137°) were put in a reaction flask and 4 cc. of concd. hydrochloric acid was added. The mixture was refluxed for twenty minutes, after which it was carefully fractionated. The last fraction contained benzene. On nitration with nitric and sulfuric acids, it yielded crystals of m-dinitrobenzene of melting point 88° and mixed m. p. 89° with a known specimen.

The non-volatile residue solidified. It was recrystallized once from alcohol, dried and analyzed for lead and chlorine. The data imply slight contamination with either diethyllead dichloride or phenyldiethyllead chloride, but they show that the salt represents triethyllead chloride for the most part.

Anal. Calcd. for $(C_2H_5)_3PbCl$: Pb, 62.8; Cl, 10.77. Calcd. for $(C_6H_5)(C_2H_5)_2PbCl$: Pb, 54.8; Cl, 9.4. Found: Pb, 61.7; Cl, 10.69, 10.71.

In another similar reaction of phenyltriethyllead (in chloroform) and hydrochloric acid, a small quantity of material separated from the hot chloroform solution. It was collected on a filter, washed, dried and analyzed. It appeared to be largely diethyllead dichloride.

Anal. Found: Pb, 59.8; Cl, 20.5.

Preparation of Lead **Tetrabenzoate.**—This compound was synthesized in essentially the manner suggested by Criegee,[13] but the following details were found to be helpful. A one-liter Claisen flask was arranged for vacuum distillation and a thermometer was placed so that the bulb dipped into the reaction mixture. Five hundred grams of benzoic acid was melted in the flask and then 155 g. of lead tetraacetate was added. Larger quantities could be used if desired. The vacuum of a water pump was used and the heating carried out so that the temperature of the mixture did not exceed 120°. The distillation temperature was from 60–80°. Most of the time the pressure was gradually dropping from 170 to 80 mm., but finally the value was 60 mm. During the course of the distillation, which required one and one-half hours, a yellow precipitate of lead tetrabenzoate separated in the molten benzoic acid. At the conclusion, most of the benzoic acid layer was decanted. This facilitated the separation of the lead tetrabenzoate from benzoic acid. For purification, the lead salt was washed with warm methanol and then with benzene. About 140 g. of the compound was obtained. The product from crystallization from benzene or even from washing with benzene appeared to retain benzene of crystallization.

Colson's observation[14] that lead tetra-salts are decomposed by alcohol was confirmed with lead tetrabenzoate. Thus, when it was boiled with methanol for a short time it went into solution to form the dibenzoate, which crystallized readily on cooling and apparently with methanol of crystallization. After drying for a week in a vacuum desiccator over phosphorus pentoxide, this alcohol was removed and the lead dibenzoate melted at 118–119°. A melting point value of 119–120° was found for lead dibenzoate which was synthesized from lead nitrate and sodium benzoate after similar crystallization from methanol and vacuum drying over phosphorus pentoxide. A mixed melting point of these two samples was 118–119°. These melting points were taken on a Maquenne block. When the usual capillary tube method was used, this lead dibenzoate melted at 107–115° with decomposition.

Anal. Subs., 0.4033, 0.4011: cc. of 0.02957 M ammonium molybdate, 30.2, 30.1. Calcd. for $(C_6H_5CO_2)_2Pb$: Pb, 46.1. Found: Pb, 45.9, 46.0.

Curiously, if any of these samples of lead dibenzoate were recrystallized from ethylene dichloride, the melting point was raised about twenty-five degrees. Thus, the value of the 118–119" material was changed to 145–147° (Maquenne block) by this process.

Pyrolysis of Lead **Tetrabenzoate.**—The pyrolysis was carried out by placing the compound in a 200-cc. round-bottomed flask which was fitted with a long air condenser. The flask was heated slowly with an oil-bath. The decomposition always took place with a mild explosion and was complete in a short time. In four experiments with 10–20 g. samples, the oil-bath temperature when vigorous decomposition occurred was 130, 148, 155 and 170". The temperature of decomposition seemed to depend somewhat on the rate of heating and somewhat on the benzene which adhered to the compound.

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[13] Criegee, *Ann.*, 481, 284 (1930).

[14] Colson, *Compt. rend.*, 136, 676, 1664 (1903).

Dense white clouds were evolved during the pyrolyses and sublimates of benzoic acid collected on the cooler parts of the flask. The residue was a sticky black *gum.* soluble in methanol. By slow evaporation and by recrystallization from dilute methanol, lead dibenzoate alone was isolated. A small sample of the residue dissolved almost completely in aqueous sodium hydroxide solution and gave no lead dioxide. Acidification of the alkaline solution with acetic acid, followed by potassium chromate solution, gave a yellow precipitate of lead chromate, indicative of Pb^{++} ion.

The pyrolytic residue was dissolved in chloroform and was apparently held in solution by the small amount of gummy impurity. After a few minutes it precipitated. From a 17-g. run, there was 14 g. of this light gray powder. Some of it was twice recrystallized from ethylene dichloride; m. p. 141–142°. A mixed melting point with lead dibenzoate of melting point 145–147" (from ethylene dichloride) was 143–144° (Maquenne block).

The chloroform filtrate from the first solution of the product was evaporated, leaving a gum. This was treated with hot ligroin (65–110°) and the hydrocarbon decanted and evaporated. This left about **0.3** g. of an oily solid which was shown to be benzoic acid. After crystallization from water and alcohol, it melted at 119–120°.

Three grams of the product from the pyrolysis was dissolved in 100 cc. of ethylene dichloride and treated with bromine (in chloroform) for about one and one-half hours. The excess bromine was evaporated and the solution filtered. Two grams of lead bromide was obtained. The filtrate was given an alkaline wash, the layers separated, and the alkaline solution was poured into cold dilute hydrochloric acid. The precipitate which formed was filtered and recrystallized from water. The first fraction, obtained by cooling slowly to room temperature, melted at 130–132" but there was not enough of this to recrystallize or characterize. After cooling in ice, a fraction of 118–119° was obtained; weight 0.1 g. The third fraction of 0.05 g. precipitated on standing overnight; m. p. 119–120'. The second and third fractions were unmistakably benzoic acid rather than a bromobenzoic acid which might have been formed had there been a C–Pb bond for the bromine to sever.

Pyrolysis of Lead Tetraacetate.—Twenty grams of lead tetraacetate was heated on an oil-bath in a 200-cc. flask which was fitted with a reflux condenser. At a bath temperature of 190°, vigorous decomposition set in. A small portion of the product, after removal from the flask, was found to dissolve completely in water. This gave tests for lead ion (bivalent) with dilute sulfuric acid and with potassium chromate solution.

By ether extracting the contents of the flask, a liquid was obtained on evaporation of the ether which was evidently acetic acid. The residue from the extraction was dissolved in water and filtered. The filter held a trace of black precipitate which was presumably lead dioxide. Almost a quantitative yield of lead diacetate was found in the filtrate. It was twice recrystallized from water, dried for twelve hours at 105°, and then crystallized from absolute alcohol; m. p. 183–187". An authentic specimen of lead acetate, twice recrystallized from absolute alcohol, melted at 187–189°. A mixed melting point determination was 184–186° (capillary tube).

Summary

Phenyltriethyllead reacts with hydrochloric acid to yield benzene and triethyllead chloride. Further reaction gives the more insoluble dichloride. Both phenyltriethyllead and tetraethyllead react readily with nitric acid to produce diethyllead dinitrate, a salt which reacts metathetically in methanol with hydrochloric acid to give the dichloride. In 0.1 *M* solution, the dinitrate is apparently 79% ionized,

On pyrolysis, lead tetrabenzoate and lead tetraacetate give rise to benzoic acid and lead dibenzoate and acetic acid and lead diacetate, respectively.

EVANSTON, ILLINOIS

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

STUDIES OF ORGANIC LEAD COMPOUNDS.
I. ACTION OF ACIDS ON LEAD ARYLS

BY PAUL R. AUSTIN[1]

RECEIVED JANUARY 26, 1931 PUBLISHED APRIL 6, 1931

In the study of the severing action of mineral acids or halogens on mixed alkyl-aryl or mixed aryl lead compounds, there appear to be two factors which determine the group that is removed. Almost invariably one of the groups of which there is the largest number is removed first.[2] As has been shown in a previous paper,[3] the electron attraction of the group in question is an even more determining factor, superseding the effect of the predominance of one of the groups, as is seen from the following example

$$(C_2H_5)_3PbC_6H_5 + HCl \longrightarrow (C_2H_5)_3PbCl + C_6H_6$$

In general, aromatic groups are replaced before aliphatic[4] and in the aromatic series (in contrast to the aliphatic) the heaviest group is replaced first.[5]

In these replacement reactions it is usually possible to replace one or two groups as desired. The removal of three groups to leave a single lead–carbon linkage in the molecule has never been accomplished. The reactions of a compound in which both the electron attraction and predominance of groups worked together should, therefore, prove to be interesting. Phenyltri-o-tolyllead was selected as being such a compound; the three *o*-tolyl groups have a greater electron attraction than the phenyl group.

Actually, the reactions of phenyltri-o-tolyllead show the strong tendency of organo-lead compounds to retain at least two lead-carbon linkages. Hydrobromic acid removed either one or two o-tolyl groups of phenyltri-*o*-tolyllead according to the concentration of the hydrobromic acid used. Nitric acid exerted a similar selective action: phenyltri-o-tolyllead in chloroform solution yielded phenyl-o-tolyllead dinitrate when treated with nitric acid. Even when the phenyltri-o-tolyllead was added to boiling concentrated nitric acid, phenyl-o-tolyllead dinitrate and di-o-tolyllead dinitrate were produced, but no single lead–carbon linkage was established.

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[1] National Research Fellow in Chemistry.

[2] Griittner and Krause, *Ber.*, 49, 1128 (1916).

[3] Hurd and Austin, THIS JOURNAL, 53, 1543 (1931).

[4] Möller and Pfeiffer, *Ber.*, 49, 2441 (1916); Griittner and Griittner, *ibid.*, 51, 1294 (1518).

[5] Krause and Schlöttig, *ibid.*, 58, 427 (1925).

The production of a mixture of products from the latter reaction is not without precedent. Triphenyl-*p*-phenetyllead yields an analogous mixture of products when treated with silver nitrate.[6]

In connection with the above study several interesting reactions were encountered. Tetra-o-tolyllead (which cannot be prepared directly from the Grignard reagent and lead chloride) was prepared by heating tri-o-tolyllead in xylene for twenty-four hours. The reaction is similar to the action of heat on triphenyllead.[7]

Attempts to prepare tri-o-tolyllead bromide by the action of bromine on tri-o-tolyllead at low temperatures were unsuccessful, probably due to the insolubility of the tri-o-tolyllead. The action of bromine on tri-*o*-tolyllead at room temperature yielded di-o-tolyllead dibromide.

The action of hydrobromic acid on tri-o-tolyllead yielded the tri-o-tolyllead bromide desired for the synthesis of phenyltri-o-tolyllead. This is a new type of synthesis of triaryl lead halides and should prove to be useful in other similar cases. The reaction also takes place in the aliphatic series,[8] but is not of importance as a method of synthesis of trialkyl lead halides.

Since the iodimetric method for the determination of lead in organo-lead compounds[9] did not appear to be suitable for this study and a volumetric method was desirable, the molybdate method for lead was adapted to the analysis of aryl lead compounds.

Experimental Part

Analytical.—A method for the analysis of lead in aryl lead compounds which has given satisfactory results has been worked out as follows. The compound was first decomposed with nitric and sulfuric acid as described by Gilman and Robinson.[10] After the lead sulfate stood for an hour with aqueous alcohol mixture, the solution was decanted through a filter and the residue was washed five times by decantation using 10-cc. portions of 1% sulfuric acid. Boiling ammonium acetate solution (15–20 cc.) was then poured through the filter paper into the beaker containing the precipitate. The filter paper was washed with boiling water containing ammonium acetate, the solution was diluted to 100 cc. and titrated hot with standard ammonium molybdate, using tannic acid as the indicator.[11] Inasmuch as a definite concentration of ammonium molybdate must be present to give the color reaction with the indicator, a blank determination should be made. The ammonium molybdate should be restandardized occasionally. This method gave satisfactory results with known tri-o-tolyllead and so was used in all of the analyses given in this paper. Analyses for bromine in the organo-lead salts were made as described by Grüttner.[12]

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[6] Krause and Schmitz, Ber., **52**, 2151 (1919).

[7] Krause and Reissaus, *ibid.*, **55**, 896 (1922).

[8] Midgley, Hochwalt and Calingaert, This Journal, **45**, 1822 (1923).

[9] Calingaert, *Chem. Reviews*, **2**, 78 (1925).

[10] Gilman and Robinson, This Journal, **50**, 1715 (1928).

[11] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons. Inc., New York, N. Y., 1924, 6th ed., Vol. II, p. 618.

[12] Grüttner, Ber., **51**, 1301 (1918).

Tri-*o*-tolyllead.—This compound has been previously prepared by Krause and Reissaus[13] and their directions were followed with some modification. To one mole of o-tolylmagnesium bromide in 400 cc. of ether, 1500 cc. of benzene and 150 g. of lead chloride were added and the whole was refluxed and stirred for five and one-half hours. The mixture was cooled and decomposed with iced ammonium chloride solution and then filtered with suction. Tri-*o*-tolyllead was extracted from the dried sludge with hot toluene. The benzene–ether layer separated from the water in the above filtrate was distilled and yielded an additional amount of product. The total yield of tri-*o*-tolyllead was 87 g. or 51% of the theoretical amount based on the o-bromotoluene used.

Tetra-*o*-tolyllead.—The preparation of this compound was carried out by refluxing 5 g. of tri-*o*-tolyllead in 130 cc. of xylene for twenty-four hours. A black precipitate of metallic lead was filtered, and refluxing again for nineteen hours did not induce further precipitation of lead. The solution was filtered again to remove a small amount of yellowish-brown precipitate and the xylene was evaporated. Recrystallization of the residue from acetone yielded 1 g. of original material (insoluble in hot acetone) and 2 g. of tetra-*o*-tolyllead. The compound was recrystallized from acetone or alcohol and melted at 201–202°.

Anal. Calcd. for $(C_7H_7)_4Pb$: Pb, 36.26. Found: Pb, 36.10, 36.07.

Phenyltri-*o*-tolyllead.—This compound was prepared by the general method described by Krause and Schmitz.[14] Eighteen grams (0.032 mole) of tri-o-tolyllead bromide was added in small portions to 0.2 mole of phenylmagnesium bromide contained in 300 cc. of ether and the mixture was stirred and refluxed for three hours. The mixture was decomposed with iced ammonium chloride solution and filtered to remove some crude phenyltri-o-tolyllead. The ether was separated and evaporated and the residue was added to the crude phenyltri-o-tolyllead obtained by filtration. The combined crude products were recrystallized from acetone or benzene, which yielded 16 g. of phenyltri-o-tolyllead. The pure compound melted at 161–162°.

Anal. Calcd. for $(C_7H_7)_3(C_6H_5)Pb$: Pb, 37.17. Found: Pb, 37.10, 37.13.

Aryl Lead Salts.—The properties of these compounds are given in Table I. The experimental conditions of the reactions varied and are recorded for each salt.

TABLE I

ARYL SALTS OF LEAD

Aryl lead salts	Yield, %	M. p., °C.	Formula	Lead, % Calcd.	Lead, % Found	Bromine, % Calcd.	Bromine, % Found
Tri-*o*-tolyl bromide	64	129–130	$(C_7H_7)_3PbBr$	36.98	36.85 36.92	14.26	14.23 14.32
Phenyldi-*o*-tolyl bromide	93	117–118	$(C_6H_5)(C_7H_7)_2PbBr$	37.93	37.84 37.90	14.63	14.59 14.58
Di-*o*-tolyl dibromide	35	150-151	$(C_7H_7)_2PbBr_2$	37.73	37.63 37.43	29.10	29.18 29.18
Phenyl-*o*-tolyl dibromide	44	116–117	$(C_6H_5)(C_7H_7)PbBr_2$	38.72	38.56 38.43	29.87	29.54 29.78
Phenyl-*o*-tolyllead dinitrate dihydrate	69-93	.....	$(C_6H_5)(C_7H_7)Pb(NO_3)_2 \cdot 2H_2O$	38.71	38.70 38.24	6.73[a]	6.59 6.79

[a] H_2O.

Tri-*o*-tolyllead Bromide.—This compound was prepared by placing 8 g. of tri-*o*-tolyllead, 150 cc. of chloroform and 9 cc. of 40% hydrobromic acid in a 200-cc. round-

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[13] Krause and Reissaus, Ber., 55, 901 (1922).

[14] Krause and Schmitz, *ibid.*, 52, 2152 (1919).

bottomed flask and shaking on a mechanical shaker for two to three hours. The mixture was filtered to remove any unreacted material and lead bromide and the chloroform separated and evaporated. The residue was recrystallized from alcohol. The product of two such reactions usually yielded 4 g. of unreacted material and 6 g. of tri-o-tolyllead bromide.

Di-o-tolyllead **Dibromide.**—(A) Five grams of tri-o-tolyllead, 150 cc. of chloroform and 10 cc. of 40% hydrobromic acid were shaken in a mechanical shaker for two hours. A clear solution resulted. The residue obtained by evaporation of the chloroform was recrystallized from alcohol. This yielded 2 g. of a mixture of tri-o-tolyllead bromide and di-o-tolyllead dibromide. Consecutive recrystallizations from aqueous alcohol and from ligroin yielded one g. of the di-o-tolyllead dibromide.

(B) Five grams of tri-o-tolyllead was dissolved and suspended in 200 cc. of chloroform. A 10% solution of bromine in chloroform was then added dropwise with stirring until the bromine color no longer disappeared. The solution was filtered to remove lead bromide and was then evaporated. Recrystallization from alcohol yielded 2 g. of di-o-tolyllead dibromide.

Phenyldi-o-tolyllead Bromide.—Six grams of phenyltri-o-tolyllead, 100 cc. of chloroform and 6 cc. of 40% hydrobromic acid were refluxed and stirred for forty-five minutes. The chloroform was separated and evaporated and the residue extracted first with a mixture of hot ligroin and absolute alcohol and then with hot alcohol. This yielded 5.5 g. of phenyldi-o-tolyllead bromide which was recrystallized from alcohol.

Phenyl-o-tolyllead **Dibromide.**—To a solution of 3.5 g. of phenyltri-o-tolyllead in 100 cc. of chloroform, 10 cc. of 40% hydrobromic acid was added and the mixture was refluxed and stirred rapidly for ninety minutes. Another 10 cc. of 40% hydrobromic acid was then added and the reaction continued for ninety minutes longer. The chloroform was separated and evaporated and the residue was recrystallized from aqueous alcohol, which yielded 1.5 g. of phenyl-o-tolyllead dibromide.

A very small amount of an unidentified by-product was obtained from this reaction. The compound is less soluble than the phenyl-o-tolyllead dibromide. It was recrystallized twice from alcohol and melted at 232° with decomposition. That the compound was not phenyllead tribromide was shown by analysis.

Anal. Calcd. for $(C_6H_5)PbBr_3$: Br, 45.75. Found: Br, 29.86.

Phenyl-o-tolyllead Dinitrate **Dihydrate.**—Three grams of phenyltri-o-tolyllead was dissolved in 100 cc. of petroleum ether (b. p. 65–110°) (chloroform was used in some reactions) and was stirred and refluxed for one hour during the slow addition of 7 cc. of nitric acid (sp. gr. 1.42). The insoluble product was filtered and weighed 2.0 g. It was recrystallized from water acidified with nitric acid.

Two grams of the above lead compound was dissolved in water and added to an aqueous solution of 3 g. of sodium bromide. The precipitate was filtered and recrystallized from aqueous alcohol, yield, 1.5 g. After three recrystallizations from aqueous alcohol the compound was pure and it was shown to be phenyl-o-tolyllead dibromide by a melting point and mixed melting point determination. About 0.2 g. of a substance which melted at 220–225° with decomposition was obtained as a by-product. This was less soluble than the main product and was undoubtedly identical with the by-product obtained above in the reaction of phenyltri-o-tolyllead and hydrobromic acid.

A more vigorous reaction was tried by adding 5 g. of phenyltri-o-tolyllead to 40 cc. of boiling nitric acid (sp. gr. 1.42). After the addition, the solution was cooled and filtered on a sintered glass funnel. Two such runs yielded 9 g. of crude product. This was recrystallized three times from water acidified with nitric acid, but the substance was not analytically pure. Three grams of the dinitrate was converted to the bromide as above; yield, 1.3 g. Repeated recrystallization from aqueous alcohol yielded two products. The larger and more soluble fraction was shown to be **phenyl-*o*-tolyl** lead dibromide by a melting point and mixed melting point. The smaller less soluble fraction was not obtained entirely pure after five recrystallizations. It melted at 144–145° and a mixed melting point with di-o-tolyllead dibromide indicated its identity with that substance. The di-o-tolyllead dibromide isolated from this reaction turned purple on exposure to light, a phenomenon not observed with the pure compound.

The author wishes to express his appreciation to Professor C. S. Marvel for his many helpful suggestions.

Summary

1. The strong tendency of organo-lead compounds to retain at least two lead-carbon linkages has been further demonstrated by the action of nitric and hydrobromic acids on phenyltri-o-tolyllead.

2. A new method for the preparation of certain triaryl lead halides has been described.

3. A new volumetric method for the determination of lead in aryl lead compounds has been developed.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

THE REACTIONS OF SOME CARBONYL COMPOUNDS WITH PHENYLHYDRAZINE

BY L. CHAS. RAIFORD AND WILBUR T. DADDOW

RECEIVED JANUARY 26, 1931 PUBLISHED APRIL 6, 1931

The interaction of phenylhydrazine with a carbonyl group joined directly to carbon and hydrogen (aldehydic) or to carbon and carbon (ketonic) is well known; but instances of this reaction are rare when the radical is situated between other elements. It is true that hydrazones corresponding to the last-named group of carbonyl compounds are known, but they are usually prepared by some method other than the direct[1] one indicated above.

The carbonyl radical in formanilide is bound directly to hydrogen and to nitrogen. A compound said to represent the hydrazone theoretically derivable from formanilide was prepared by Zwingenberger and Walther[2]

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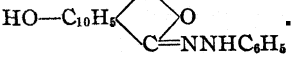
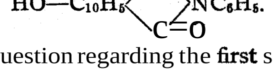
[1] The structure assigned by Anselm and Zuckmayer [Ber., 32, 3294 (1899)] to the hydrazone obtained by direct action of phenylhydrazine on hydroxynaphthalic anhydride is,



. In the same paper the anilide is represented by the symmetrical structure,



Reasons for these differences are not given, which raises a question regarding the first structure.

[2] Zwingenberger and Walther, J. prakt. *Chem.*, [2] 57,223 (1898).

by heating methenyldiphenylamidine with an excess of phenylhydrazine. They recorded a melting point of 90–91°. Worrall[3] heated equimolecular proportions of phenylhydrazine and thiodiacetoacetylanilide and obtained a product melting at 126–127°. He recorded it as the hydrazone of formanilide. In the present work in an attempt to use the direct method, formylphenylhydrazine, m. p. 143–144°,[4] was obtained by heating a mixture of formanilide, phenylhydrazine and acetic acid.[5] The same product was obtained when formanilide was substituted by 4-bromo-, 2-, 3-, and 4-nitroformanilides, and by o- and *p*-formotoluidides, which indicates that the reaction is probably general. In each case the corresponding aniline was recovered.

A compound in which the carbonyl radical is joined directly to two nitrogen atoms is diphenylurea. Its behavior toward phenylhydrazine was next studied. When an alcoholic solution of equimolecular proportions of these compounds was heated for two days in an open vessel no new product could be detected. Repetition of the experiment in the presence of acetic acid failed to cause any change. After the mixture had been heated for thirty days, only starting material could be isolated. To test the possibility of reaction under different conditions, a mixture of diphenylurea with 1.2 molecular proportions of phenylhydrazine was heated in a sealed tube at 80–90° for seventy days. This gave 1,4-diphenylsemicarbazide; m. p. 176°. The use of an alcoholic solution of the reactants in another experiment gave almost the theoretical yield of the same product. It was identified by a mixed melting point determination with the semicarbazide prepared by the interaction of phenylhydrazine and phenyl isocyanate.[6]

It is known that certain sulfur compounds are more reactive than their oxygen analogs. Thus, Tiemann[7] found that coumarin, which contains a carbonyl radical, does not react with phenylhydrazine, while thiocoumarin does so to give the corresponding hydrazone. In the present study an attempt was made to prepare a phenylhydrazone from diphenylthiourea by refluxing an alcoholic solution of the latter with phenylhydrazine. The crystalline solid that separated on cooling melted at 178°. Aniline was isolated from the filtrate and identified by conversion into acetanilide. The other product was found by mixed melting point determination and other properties to be identical with 1,4-diphenylthiosemicarbazide,[8] m. p.

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[3] Worrall, THIS JOURNAL, 42, 1058 (1920).

[4] Just [*Ber.*, 19, 1201 (1886)] reported 145° for a product obtained by heating formamide and phenylhydrazine.

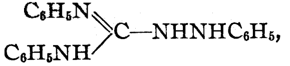
[5] Not obtained in the absence of the acid.

[6] Kuhn [*Ber.*, 17, 2884 (1884)] reported 170° as the melting point.

[7] Tiemann, *ibid.*, 19, 1666 (1886); Meyer and Jacobson, "Lehrbuch der organischen Chemie," Veit, Leipzig, 1902, Bd. II, Th. I, p. 676.

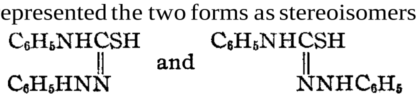
[8] This compound was first isolated by Fischer [*Ann.*, 190, 122 (1878)], who obtained it by mixing equimolecular proportions of phenyl mustard oil and phenylhydrazine in

178–179°, prepared by the action of phenylhydrazine on phenyl mustard oil. It was further identified by conversion into a mercury salt,[9] which was readily decomposed by hydrogen sulfide. Apparently this action of phenylhydrazine on thioureas is general, as indicated in Table I.

When a solution of phenylhydrazine and a thiourea is heated in the presence of a desulfurizing agent such as lead oxide, a guanidine derivative is formed. L. Marckwald[10] boiled an alcoholic solution of equimolecular proportions of thiocarbanilide and phenylhydrazine with an excess of lead oxide until desulfurization was complete. The product melted at 138–139°, and was assigned the structure required by the hydrazone of diphenylurea, $(C_6H_5NH)_2C{=}NNHC_6H_5$ (I). The same structure was assigned by Wessel[11] to a product that melted at 204°, which he obtained by heating at 120° an equimolecular mixture of carbodiphenylimide and phenylhydrazine, and which he named phenylhydrazone carbodiphenylamine or hydrazone base. W. Marckwald and Wolff[12] also used this structure for a product that melted at 160°, and which was obtained by boiling an alcoholic solution of either of the stereoisomeric diphenylthiosemicarbazides mentioned above with aniline and lead oxide until desulfurization was complete. Their product could also be represented by formula (11),  $\genfrac{}{}{0pt}{}{C_6H_5N}{C_6H_5NH}\!\!>\!C{-}NHNHC_6H_5$, which indicates a hydrazine rather than a hydrazone. The choice between these formulas involves both the method of preparation and the properties of the compounds.

Though these guanidine derivatives can be prepared from the thioureas in one operation, as indicated above, it was found in the present work that Busch's[13] method, which involves the preparation of the carbodiphenylimide in the pure form and subsequent treatment of this with phenylhydrazine, gives the highest yield. Incidentally, this proves that the imide is the intermediate product in Marckwald's method. The behavior

"not too dilute" alcoholic solution. He reported a melting point of 177°. W. Marckwald [*Ber.*, 25, 3106 (1892)] found that at a lower temperature the reaction gave a labile form, m. p. 139°, which may be isomerized by heat or treatment with acid into a stable form, m. p. 176°. He represented the two forms as stereoisomers



$$\begin{array}{c} C_6H_5NHCSH \\ \| \\ C_6H_5HNN \end{array} \quad \text{and} \quad \begin{array}{c} C_6H_5NHCSH \\ \| \\ NNHC_6H_5 \end{array}$$

(labile) (stable)

[9] Though the product here in question was obtained in but one form, the fact that it gave a mercury salt may possibly be regarded as support for Marckwald's hydrosulfide structure. *Anal.* Subs., 0.1471: HgS, 0.0487. Calcd. for $(C_{13}H_{13}N_3S)_2Hg$: Hg, 29.15. Found: Hg, 28.50.

[10] L. Marckwald, "Das Phenylhydrazin and seine Derivate," Thesis, Berlin, 1888, p. 39.

[11] Wessel, *Ber.*, 21, 2272 (1888).

[12] W. Marckwald and Wolff, *ibid.*, 25, 3116 (1892).

[13] Busch, *ibid.*, 38, 858 (1905).

of the imide toward other reagents shows that the normal reaction involves addition at one double bond, and tends to support Formula II for the product obtained when it adds phenylhydrazine. Thus, Weith[14] found that carbodiphenylimide may add one molecular proportion of hydrogen chloride. Lengfeld and Stieglitz[15] showed' that this product reacts with sodium ethylate to give the ethyl ether of isodiphenylurea, which they obtained, also, by direct addition of alcohol to the diimide at an elevated temperature lander pressure. Formula I would require addition at both double bonds,

If the guanidine derivatives under consideration are represented by Formula I they would be hydrazones and should not reduce Fehling's solution.[16] They do reduce it slightly at the boiling point. Again, if these products are hydrazones, oxidizing agents should convert them into tetrazones, as observed by Pechmann and Runge[17] and the molecular weights of the products should be practically double those of the starting materials. The compounds here under consideration were oxidized by mercuric oxide to new substances, but molecular weight determinations showed no difference between starting material and product, which is in accordance with the behavior expected if the starting material is represented by Formula II. Here the loss of hydrogen should occur from adjacent hydrogen atoms in the same molecule to give an azo compound. Azo compounds were obtained.

Experimental Part

Sym.-di-(2,5-dibromophenyl)-thiourea.—Dyson, George and Hunter[18] recorded 154° as the melting point of the thiourea obtained by the action of thiocarbonyl chloride on the required dibromoaniline. In the present work the urea was first prepared by boiling an alcoholic solution of the aniline, carbon disulfide and sodium hydroxide for fourteen hours. Crystallization from benzene gave colorless needles; m. p. 191°. A second portion prepared according to Fry's[19] directions melted at 191°, as did a third sample obtained by the action of thiocarbonyl chloride, mentioned above.

Anal. Subs., 0.1718: 6.30 cc. of 0.1 N HCl. Subs., 0.2054: AgBr, 0.2828. Calcd. for $C_{13}H_8N_2Br_4S$: N, 5.14; Br, 58.82. Found: N, 5.14; Br, 58.60.

Sym.-di-(2,4-dibromophenyl)-thiourea.—To a solution of 8 g. of pyridine and 9.3 g. of 2,4-dibromoaniline, prepared as directed by Chattaway and Clemo,[20] in 100 cc. of carbon disulfide, there was added a solution of 6.4 g. of iodine in 50 cc. of carbon disulfide. After two hours, when the color of iodine had disappeared, the mixture was dis-

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[14] Weith, *Ber.*, 7, 11 (1874).

[15] Lengfeld and Stieglitz, *ibid.*, 27, 926 (1894).

[16] Strache's [*Monatsh.*, 12,528 (1891)] quantitative method for the determination of the carbonyl radical depends on the non-activity of phenylhydrazone toward Fehling's solution.

[17] Pechmann and Runge, *Ber.*, 27,2920 (1894).

[18] Dyson, George and Hunter, J. *Chem. Soc.*, *443* (1927).

[19] Fry, THIS JOURNAL, 35,1543 (1913).

[20] Chattaway and Clemo, J. *Chem. Soc.*, 109, 90 (1916).

tilled with steam, the non-volatile residue collected, washed with alcohol and with water. Two crystallizations from benzene gave fine needles; m. p. 203°.

Anal. Subs., **0.3489:** AgBr, **0.4814.** Calcd. for $C_{13}H_8N_2Br_4S$: Br, **58.82.** Pound: Br. **58.72.**

Preparation of Thiosemicarbazides.—With the exceptions noted below, the general method here used was as follows: **10** g. of the required urea was suspended in alcohol, a slight excess of phenylhydrazine was added, the mixture was boiled under a reflux condenser for about six hours, and then poured into water. The method was first tested by the preparation of derivatives from phenyl-, m- and *p*-tolyl, and β-naphthylureas, which had previously been obtained by the interaction of the required amine and mustard oil. after which a number of new ones were studied. In most instances the products were readily purified by crystallization from alcohol, from which they separated as colorless needles. Physical constants and analytical data are given in Table I.

TABLE I

THIOSEMICARBAZIDES

			Analyses			
			Nitrogen, %		Sulfur. %	
Name	Formula	M. p., °C.	Calcd.	Found	Calcd.	Found
1-Phenyl-4-(4-bromophenyl)	$C_{13}H_{12}N_3BrS$	179–180	13.05	13.08[f]	9.93	9.70
1-Phenyl-4-(2,5-dibromophenyl)[a]	$C_{13}H_{11}N_3Br_2S$	188	10.47	10.54	...	...
1-Phenyl-4-(2,4-dibromophenyl)[b]	$C_{13}H_{11}N_3Br_2S$	177–178	...	...	...	...
1-Phenyl-4-(*o*-tolyl)[c]	$C_{14}H_{15}N_3S$	170–171	16.34	16.32	...	...
1-Phenyl-4-(*m*-tolyl)[d]	$C_{14}H_{15}N_3S$	173–174	16.34	16.28	...	...
1-Phenyl-4-(α-naphthyl)[e]	$C_{17}H_{15}N_3S$	192–193	14.33	14.07	10.92	10.90
1-Phenyl-4-(3-nitrophenyl)	$C_{13}H_{12}O_2N_4S$	172	...	...	11.11	11.16

[a] The composition was also checked by analysis for bromine. *Anal.* Subs., **0.1534:** AgBr, **0.1429.** Calcd. for $C_{13}H_{11}N_3Br_2S$: Br, **39.90.** Found: Br, **39.65.**

[b] Composition checked for halogen content. Anal. Subs., **0.1559:** AgBr, **0.1454.** Calcd. for $C_{13}H_{11}N_3Br_2S$: Br, **39.90.** Found: Br, **39.69.**

[c] Obtained previously by interaction of phenylhydrazine and o-tolyl mustard oil by Dixon [*J.* Chem. *Soc.*, *57*, **258 (1890)**], who reported a melting point of **162–163°.** In the present work a solution of **10** g. of the required thiourea and **5** g. of phenylhydrazine in **250 cc.** of benzene was evaporated at its boiling point to a volume of about **25 cc.** and allowed to cool.

[d] Reported by Bose and Ray-Chaudhury [*J. Ind.* Chem. *Soc.*, **4, 261 (1927)**], who prepared it by the action of m-tolyl mustard oil on phenylhydrazine. Here prepared by the method given above for the ortho isomeride.

[e] Checked by analysis because the product obtained by Dixon [J. Chem. *Soc.*, 61, **1019 (1892)**] through the action of phenylhydrazine on a-naphthyl mustard oil and supposed to be identical with this one, was recorded as melting at **183°.**

[f] Kjeldahl method was modified as directed by Milbauer [*Z.* anal. Chem.. **42, 728 (1903)**] in order to avoid loss of nitrogen.

Preparation of **Carbodiphenylimides.**—A mixture of **20** g. of the thiourea, **30** g. of lead oxide and **500 cc.** of benzene was refluxed until a filtered portion no longer darkened a fresh portion of oxide, the whole filtered, the solvent distilled off until about **40–50** cc. remained, and the residue allowed to stand. The product was then purified in a suitable way. Data for the new ones thus obtained are given in Table II.

Preparation of Diphenylanilguanidines.—Ten grams of the required **carbodiphenylimide** was dissolved in about **250** cc. of benzene, the necessary amount of phenylhydrazine added, the liquid evaporated to about **25 cc.** and allowed to stand. The resulting

TABLE II

CARBODIIMIDES

Name	Formula	M p , °C.	Nitrogen, % Calcd	Nitrogen, % Found
Carbodi-(m-tolyl)	$C_{15}H_{14}N_2$	118–119[a]	12.61	12.72
Carbodi-(2-bromophenyl)	$C_{13}H_8N_2Br_2$	98–100	7.95	7.83
Carbodi-(4-bromophenyl)	$C_{13}H_8N_2Br_2$	144[b]	7.95	7.91
Carbodi-(2,4-dibromophenyl)	$C_{13}H_6N_2Br_4$	156–157[c]	5.49	5.48
Carbodi-(2,5-dibromophenyl)	$C_{13}H_6N_2Br_4$	172–173[d]	..	..

[a] The residue left after evaporation of the solvent used in the method of preparation described above did not solidify on standing. Most of it boiled at 218° under **24** mm., and this distillate solidified within twenty-four hours.

[b] Ingold [*J. Chem. Soc.*, 125, 101 (1924)] obtained by a different method a product having the composition of this one and recorded it as a yellow viscous liquid boiling at 202" and 10 mm. The product here in question has not been reported, and is probably a polymer of Ingold's compound. Unsubstituted carbodiphenylimide was obtained by Weith [*Ber.*, 7, 10 (1874)] in both the oily and the solid forms, and Miller and Plochl [*Ber.*, 28, 1007 (1895)] argue that the latter is a polymer of the former.

[c] Obtained as colorless needles from alcohol.

[d] Attempts to crystallize from benzene gave small compact globules that were crystalline in structure. Bromine content agrees with the formula given. *Anal.* Subs., 0.1985: AgBr, 0.2913. Calcd. for $C_{13}H_6N_2Br_4$: Br, 62.74. Found: Br, 62.46.

solid was purified in a suitable way.[21] Data for these derivatives are given in Table III.[22]

TABLE III

ANILGUANIDINES[e]

Name	Formula	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
Di-(*o*-tolyl)	$C_{21}H_{22}N_4$	137"	16.96	16.93
Di-(m-tolyl)	$C_{21}H_{22}N_4$	158–159[b]	16.96	16.92
Di-(2-bromophenyl)	$C_{19}H_{16}N_4Br_2$	147–148'	12.17	12.08
Di-(3-bromophenyl)	$C_{19}H_{16}N_4Br_2$	162–163[c]	12.17	12.05
Di-(4-bromophenyl)	$C_{19}H_{16}N_4Br_2$	202–203"	12.17	12.29
Di-(a-naphthyl)	$C_{27}H_{22}N_4$	157–159[d]	13.93	13.96
Di-(β-naphthyl)	$C_{27}H_{22}N_4$	181–182[c]	13.93	13.90

[a] Colorless prisms from benzene. [b] Faintly colored prisms from benzene. [c] Colorless, fine needles from benzene. [d] Four recrystallizations from benzene failed to give a product with constant melting point. [e] All these products become colored more or less rapidly when exposed to air.

Preparation of the Azo Compounds.—The method was tested by starting with the unsubstituted diphenylanilguanidine isolated by Marckwald and Wolff. Five grams of the compound was dissolved in about 10 cc. of hot alcohol, an excess of mercuric oxide

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[21] During crystallization these products often become colored, due probably to oxidation. To prevent this change Marckwald and Wolff[12] passed hydrogen sulfide into the crystallizing mixture. In the present work such treatment was avoided, because tests showed that when it was used the final product was contaminated with sulfur.

[22] It is of interest to note that no guanidine derivative was obtained from a diphenylimide which contained two bromine atoms in a single phenyl nucleus. This failure does not seem to be explainable in terms of steric hindrance. It will be studied further.

added, the mixture boiled for five to ten minutes, filtered and the azo compound isolated from the filtrate in a suitable way. The product showed the properties recorded in the literature. To show that it was not a tetrazone the molecular weight was determined.[23]

(a) 0.0297 g. of substance dissolved in 0.6172 g. camphor, A = 6.7"

$$\text{Molecular weight} = \frac{(40{,}000)\ (0.0297)}{(0.6172)\ (6.7)} = 287$$

(b) 0.0281 g. of substance dissolved in 0.6878 g. camphor, A = 5.5"

$$\text{Molecular weight} = \frac{(40{,}000)\ (0.0281)}{(0.6878)\ (5.5)} = 297$$

Calcd. for $C_{19}H_{16}N_4$: mol. wt., 300. Found: 287. 297.

Other compounds indicated in Table IV were obtained in the same way.

Table IV

Azo Compounds from Anilguanidines

Name	Formula	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
Di-(*o*-tolyl)	$C_{21}H_{20}N_4$	113–114[a]	17.07	17.03
Di-(m-tolyl)	$C_{21}H_{20}N_4$	107–108[b]	17.07	17.10
Di-(2-bromophenyl)	$C_{19}H_{14}N_4Br_2$	132–133"	12.22	12.11
Di-(3-bromophenyl)	$C_{19}H_{14}N_4Br_2$	131–132[d]	12.22	12.17
Di-(4-bromophenyl)	$C_{19}H_{14}N_4Br_2$	163–164"	12.22	12.22

[a] Pale red needles from alcohol. [b] Brilliant red needles from alcohol. [c] Crystallization from alcohol gave brilliant red needles that soften at about 129" if heated slowly. [d] Obtained as dull red needles when the hot saturated alcoholic solution was diluted with hot water until precipitation began, and then allowed to cool. [e] Red crystalline material from the alcoholic filtrate of the reaction mixture.

Summary and Conclusions

1. The carbonyl radical in formanilide does not condense with phenylhydrazine to give a hydrazone under the conditions studied. The products are aniline and formylphenylhydrazine. Substitution products of formanilide react similarly.
2. Diphenylurea reacts with phenylhydrazine to give a semicarbazide and eliminates aniline. The corresponding thiourea behaves in the same way.
3. Several new carbodiphenylimides have been prepared and studied. With the exception of the 2,4- and 2,5-dibromo compounds, the imides added phenylhydrazine to give the corresponding anilguanidines. These failures are not explainable on the theory of steric hindrance.
4. The evidence indicates that these guanidine derivatives are not hydrazones.
5. Further work is in progress.

Iowa City, Iowa

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[23] Rast, *Ber.*, 55, 3727 (1922).

[CONTRIBUTION NO. 438 FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND COMPANY]

THE REACTION BETWEEN BARBITAL (DIETHYLBARBITURIC ACID) AND PHOSPHORUS PENTACHLORIDE

BY ARTHUR W. DOX[1]

RECEIVED JANUARY 28, 1931 PUBLISHED APRIL 6, 1931

The 5,5-dialkylbarbituric acids, of which barbital is the oldest and most familiar example, are surprisingly inert chemically despite their powerful physiological action as hypnotics. Barbital is one of the least reactive members of the series, presumably because of a molecular stability conferred by its paired ethyl groups. It is resistant to most oxidizing and reducing agents, to high temperatures, and is not easily hydrolyzed. Aside from its imide hydrogen it may be said to possess no functionally reactive groupings. Consequently very few derivatives have been prepared from it. These few comprise desoxyveronal,[2] a xanthydrol condensation product,[3] the Grignard reaction products,[4] and several N-alkyl derivatives[5] These represent practically all the derivatives that have been prepared directly from a 5,5-dialkylbarbituric acid without breaking open the pyrimidine ring.

In view of the fact that other pyrimidones have been converted into corresponding chloropyrimidines by means of phosphorus oxychloride and pentachloride, it seemed reasonable to expect that barbital would undergo the same reaction. Our purpose was to replace the three oxygens by six chlorines, two of which would then split off as hydrogen chloride, leaving a tetrachloropyrimidine derivative with paired ethyls in the 5-position; and then to replace the four chlorines by hydrogen and obtain the structural base, *viz.*, 5,5-diethyldihydropyrimidine. The first of the above reactions was successfully accomplished and the tetrachloro derivative obtained beautifully crystalline. The yield, however, was small, due to a side reaction of an intermediate chlorination product. Removal of the four chlorines to obtain the structural base has thus far been unsuccessful because of the ease with which the tetrachloro derivative is hydrolyzed by water alone into a nitrile. An unexpected reaction occurs here. Hydrogen chloride is split off quantitatively, but the pyrimidine ring then breaks down into diethylmalononitrile and presumably water and carbon dioxide. In the presence of zinc dust there is formed also a diethyldichloropyrimidine by replacement of two chlorines by hydrogens. This substance is much

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[1] Most of the analyses reported in this paper were made by Dr. I. W. Grote of this Laboratory, using the Pregl micro technique.

[2] Tafel and Thompson, Ber., 40,4489 (1907).

[3] Fabre, J. *pharm. chim.*, 26,241 (1922).

[4] Dox, THIS JOURNAL, 49,2275 (1927).

[5] Dox and Jones, *ibid.*, 51,316 (1929); Lyons and Dox, *ibid.*, 51,288 (1929).

more stable and may be steam distilled without decomposition. It is also resistant to further reduction, so that our attempts thus far to replace the two remaining chlorines by hydrogen have not been successful.

Experimental

In the first attempts to chlorinate barbital, phosphorus oxychloride was used. The parent barbituric acid had previously been converted into trichloropyrimidine.[6] by heating for one hour in a sealed tube at 130–140° with phosphorus oxychloride. Under these conditions barbital failed to react. Even when the temperature was raised to 175–180° and the heating prolonged six hours, there was very little evidence of reaction. The barbital was recovered almost quantitatively and identified by its melting point. The only indication of a slight reaction was a terpene-like odor of the steam distillate obtained after decomposition of the phosphorus oxychloride by pouring the reaction mixture on ice.

2,4,6-Trichloro-5-*sec.*-butylpyrimidine.—The stability of the dialkylbarbituric acids. as illustrated by barbital, toward phosphorus oxychloride is in striking contrast to the readiness with which a monoalkylbarbituric acid reacts. A tube containing 5 g. of *sec.*-butylbarbituric acid and 15 cc. of phosphorus oxychloride was heated at 175–180° simultaneously with the barbital in the preceding experiment. The reaction mixture was poured on ice and after decomposition of the excess phosphorus oxychloride the residual oil was extracted with ether. Evaporation of the solvent then left a white crystalline mass which after recrystallization from alcohol melted at 40°. The yield was 5.157 g. from 5 g. of *sec.*-butylbarbituric acid, or 79% of the theoretical.

Anal. Calcd. for $C_8H_9N_2Cl_3$: N, 11.69; Cl, 44.47. Found: N, 11.65, 11.53; Cl, 44.53.

As pointed out by Behrend,[7] in the analogous reaction with methyluracil, each oxygen atom is evidently replaced by two chlorines, then one chlorine from each pair is split out with an adjacent hydrogen as hydrogen chloride, leaving three double bonds in the ring.

A lower homolog, 2,4,6-trichloro-5-ethylpyrimidine, has been prepared by v. Merkatz[8] from 5-ethylbarbituric acid and phosphorus oxychloride.

Reaction with Barbital

In subsequent experiments with barbital, phosphorus pentachloride was used in place of phosphorus oxychloride because of its greater reactivity. Even here the reaction appears to reach an equilibrium, so that phosphorus pentachloride and unreacted barbital are still present although the mixture may have been heated for two or three days after the evolution of hydrogen chloride had ceased. The phosphorus pentachloride exchanges 2Cl for each O of the barbital, and the resulting phosphorus oxychloride can for the most part be removed readily by distillation. It is unlikely that complete chlorination of the barbital molecule occurs before the splitting out of hydrogen chloride begins. If the reaction proceeds stepwise and in a definite sequence, replacement of oxygen being followed by removal of hydrogen chloride, there would be four intermediate products between Formulas II and VI. It is obvious that one of the carbons must retain both its chlorines, since there are three pairs of chlorines but only two adjacent hydrogens. The final product would be a tetrachloro derivative with two

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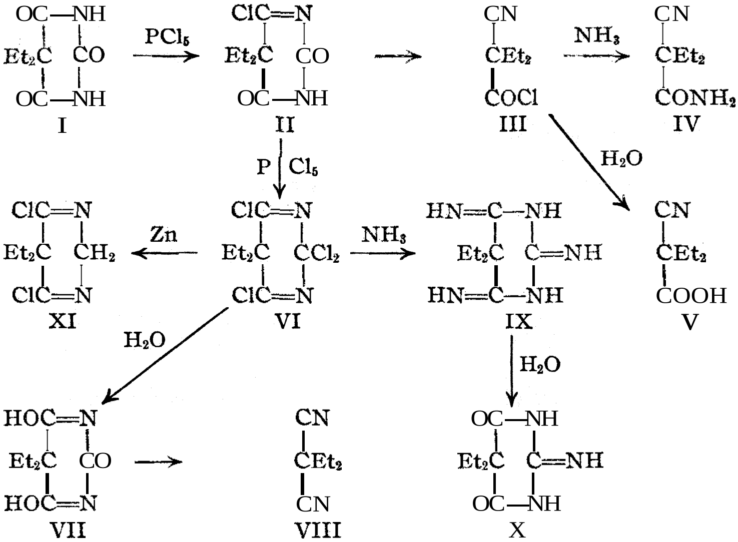
[6] Gabriel, Ber., **33**, 3666 (1900).

[7] Behrend, *Ann.*, **227**, 25 (1885).

[8] v. Merkatz, Ber., 52,869 (1919).

double bonds, instead of a trichloro derivative with three double bonds as illustrated by the *sec.*-butyl compound above.



Theoretical proportions for this reaction would be $3PCl_5$ to 1 barbital. Actually this represents an excess of phosphorus pentachloride, for the reason that the reaction does not proceed entirely in this manner. Another and entirely different reaction occurs simultaneously, yielding a product which retains one of the barbital oxygens. This will be discussed presently.

In the case of barbituric acid or its monoalkyl derivatives only the first of these reactions seems to occur. The reaction mixture may be poured on ice to decompose the remaining phosphorus chlorides, and a good yield of the chlorinated pyrimidine thus obtained. With barbital, however, a viscous product remains which reacts slowly with water and has the characteristic odor of organic acid chlorides. In the first experiments where the reaction mixture, after hydrolysis of the phosphorus chlorides, was extracted with ether and the tetrachloropyrimidine derivative crystallized by evaporation of the solvent, a viscous mother liquor remained. Distillation of this with steam gave an oily product with a strong camphoraceous odor. The oil solidified in crystals, melting at 44°, which were identified as diethylmalononitrile, while extraction of the aqueous layer with ether gave a crystalline substance which was identified as diethylcyanoacetic acid. These obviously were secondary products formed during the steam distillation. In subsequent experiments steam distillation was therefore avoided.

A number of chlorinations were made, using barbital and phosphorus pentachloride. In several of these a small quantity of phosphorus oxychloride was added to moisten the mixture but no advantage appeared to be gained by so doing. The following experiment was performed on a somewhat larger scale and illustrates the typical reaction.

An intimate mixture of 96 g. of barbital and 376 g. of phosphorus pentachloride was placed in a 1-liter distilling flask connected with a downward condenser and receiver, the latter provided with an outlet tube leading through dry calcium chloride and terminating over a quantity of water contained in a flask. The mixture was heated by immersing the distilling flask in an oil-bath maintained at 115–120°. The mass slowly sintered while a vigorous evolution of hydrogen chloride occurred. The hydrogen chloride was absorbed by the water beneath the end of the outlet tube. After six hours' heating the mass had become liquid and the evolution of gas had practically ceased. On cooling overnight the excess phosphorus pentachloride formed a crystalline crust on the walls of the flask. Titration of an aliquot of the hydrogen chloride collected indicated the equivalent of 40.8 g. compared to a theoretical value of 38.1 g., hence the escaping vapors had carried over some of the phosphorus oxychloride. The apparatus was then connected to a water pump and the bath gradually warmed. At first more hydrogen chloride came off at 65 mm. and bath temperature of 55–60°. At 80° and 80 mm. distillation of the phosphorus oxychloride began. At 110° and 80 mm. the distillation was practically complete and the sublimation of phosphorus pentachloride began. The phosphorus oxychloride thus collected weighed 45.5 g. This does not represent the entire yield since no attempt was made at quantitative recovery by providing adequate cooling. Atmospheric pressure was then restored and the bath temperature raised to 135° for four hours to insure as complete a reaction as possible. The reaction mixture was again cooled overnight, and the viscous amber-colored liquid was filtered through dry asbestos to remove the phosphorus pentachloride that had separated. The filtrate was collected directly in a Claisen distilling flask.

Distillation of this filtrate gave a further yield of phosphorus oxychloride. Between 50 and 55° at 65 mm. 25 g. was collected, and a further sublimation of phosphorus pentachloride occurred. Distillation was then continued at 5–6 mm. pressure, 20.6 g. of colorless liquid passing over between 60 and 80°. Although the bath temperature was raised to 150°, no more distillate was obtained. The bath was then removed and the flask carefully heated over a free flame. Practically no further distillate was thus obtained, but a rise of mercury in the manometer from 5 to 15 mm. indicated an incipient decomposition, hence the distillation was discontinued.

Diethylcyanoacetyl Chloride (Formula III).—The distillate thus obtained had the characteristic odor of organic acid chlorides, and a test portion treated with water slowly decomposed with liberation of acid. Owing to the difficulty of removing traces of phosphorus chlorides the product was not analyzed, but was converted into crystalline derivatives for identification.

Diethylcyanoacetamide (Formula IV).—The above distillate was dissolved in 300 cc. of benzene and saturated with dry ammonia. A copious separation of ammonium chloride was filtered off and washed with ether. Evaporation of the combined mother liquor and washings left a white crystalline residue which on recrystallization from hot water gave long needles (5 cm.) melting at 121°.

Anal. Calcd. for $C_7H_{12}ON_2$: N, 20.0. Found: N, 19.81.

Diethylcyanoacetic Acid (Formula V).—Another portion of the distillate was distilled with steam and the distillate extracted with ether. Evaporation of the solvent and recrystallization of the residue by dissolving in benzene and adding petroleum ether gave a crystalline product, very soluble in water, alcohol and benzene, strongly acid and melting at 68°.[9]

Anal. Calcd. for $C_7H_{11}O_2N$: N, 10.07. Found: N, 9.93. Mol. wt. by titration, 143; calcd., 141.

2,2,4,6-Tetrachloro-5,5-diethyldihydropyrimidine (Formula VI).[10]—The undistilled

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[9] The melting point of diethylcyanoacetic acid is given by Hesse (*Am. Chem. J.*, 18, 748 (1896), as 57°, and by Hessler, THIS JOURNAL, 38, 939 (1916), as 61°.

[10] The difference in conjugated structure between this substance and the 2,4,5,6-tetrachloropyrimidine prepared by Ciamician and Magnaghi, [*Ber.*, 18, 3444 (1885)] from alloxan and by Emery, [*Ber.*, 34, 4178 (1901)] from dialuric acid will be seen by a glance at the formula.

residue from the diethylcyanoacetyl chloride was orange-red in color and quite viscous. On two days' standing it deposited a mass of crystals which were then collected on a large frit filter and washed with a little petroleum ether, then with methyl alcohol which removed the sticky mother liquor. The alcohol washings were collected separately and discarded. White rhombic crystals remained which melted at 127° and showed no change in melting point after recrystallization from ethyl alcohol.

Anal. Calcd. for $C_8H_{10}N_2Cl_4$: Cl, 51.45; N, 10.14. Found: Cl, 51.14; N, 10.19.

The yield in the first crop was 14.2 g. and a second crop of 9.3 g. was obtained by allowing the filtrate, diluted with petroleum ether, to stand for two days. The mother liquor was further diluted with petroleum ether (10 vols.) and treated with dry ammonia, avoiding an excess. After removal of the ammonium chloride by filtration, small amounts of both diethylcyanoacetamide and the tetrachloropyrimidine were obtained by evaporation of the solvent.

Diethylmalononitrile (Formula VIII).—Steam distillation of the final mother liquor gave an oily product which presently solidified and had a strong camphoraceous odor. This came over (about 1 g.) in the first few cc. of distillate and was collected separately. It melted at 44° and was quite volatile.

Anal. Calcd. for $C_7H_{10}N_2$: N, 22.95. Found: N, 23.0.

It is obviously a product formed in the steam distillation, since in no case was it otherwise obtained or its odor detected. Further distillation with steam yielded about 1 g. of the tetrachloropyrimidine, m. p. 127°, which solidified completely in the condenser.

The residue in the distilling flask consisted of a slightly turbid aqueous solution and a brown gummy mass. When clarified with charcoal and evaporated, the aqueous solution yielded about 1 g. of barbital crystals, identified by melting point and taste.

5,5-Diethylmalonylguanidine (Formula X).—The precipitate of ammonium chloride from the ammonia treatment of the second mother liquor from the tetrachloropyrimidine was gummy and evidently contained other reaction products. Extraction of the ammonium chloride with water left a brown gummy mass which dried overnight to a porous brittle mass. Treatment of this with ether dissolved all but a white crystalline powder, insoluble in water and in ether, very slightly soluble in alcohol. By crystallizing from a large volume (1.5 liters) of hot alcohol it was obtained in colorless needles which did not melt when heated to 270°. The substance was readily soluble, however, in dilute acids and alkalies and was reprecipitated by neutralizing the solution.

Anal. Calcd. for $C_8H_{13}O_2N_3$: C, 52.46; H, 7.10; N, 22.95. Found: C, 52.6, 52.7; H, 6.7, 7.1; N, 23.0, 23.3.

The yield was 2.3 g. This substance has been prepared by Fischer and Dilthey[11] from ethyl diethylmalonate and guanidine.

Evaporation of the ether used in the above extraction gave a further separation of barbital. In fact, small quantities of barbital were frequently encountered at various stages of the process of working up the reaction products, especially in mother liquors that had been given a final treatment with water or in residues from steam distillation. It is possible that its presence indicates a regeneration of barbital by hydrolysis of the tetrachloropyrimidine or partially chlorinated intermediate products. On the other hand, it is equally probable that the chlorination is not strictly quantitative and that some of the original substance remains unaltered despite the excess of phosphorus pentachloride used.

A yellowish-brown amorphous residue finally remained from which we were unable to obtain any definitely crystalline substance. On the basis of the total amount of tetrachloro derivative actually isolated (24.5 g.), and the crude diethylcyanoacetyl

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[11] Fischer and Dilthey, *Ann.*, 334,352 (1904).

chloride (**20.6** g.) from which the corresponding amide and acid were prepared, these substances evidently constitute the main reaction products. They are formed in nearly equal quantities under the conditions of our experiments and together account for approximately 46% of the barbital used. In neither case, however, was the recovery quantitative, as was shown by the further isolation of their derivatives from mother liquors.

The formation of a nitrile acid chloride (diethylcyanoacetyl chloride) by the action of phosphorus pentachloride on a cyclic urea such as barbital was at first rather puzzling because no such reaction had been recorded as occurring in the chlorination of numerous purine and pyrimidine derivatives. An interesting parallel, however, was found in the work of Bredt and Iwanoff,[12] who obtained a nitrile acid chloride from phosphorus pentachloride and camphoric imide. The same pyridone ring is present in both glutaric and camphoric imide, but only the latter undergoes this reaction. Now barbital and camphoric imide not only have an imide grouping in common, but both contain also a paired alkyl grouping and in that respect differ from their parent substances which yield only a stable chlorinated ring. The mechanism of the reaction in the case of barbital is not as simple as that proposed by Bredt and Iwanoff for the camphoric imide reaction, since the ring has to break at two places. In the barbital reaction their hypothesis could be applied to the formation of the nitrile grouping, but the formation of acid chloride requires a cleavage by hydrogen chloride. The products would then be diethylcyanoacetyl chloride and carbamyl chloride. The latter boils at 61–62° and would pass off with the hydrogen chloride and phosphorus oxychloride in the first distillate. It may be assumed that the nitrile acid chloride is formed from an intermediate chlorination product, e. g., Formula 11, where one of the malonyl carbonyls is still present.

4,6-Dichloro-5,5-diethyldihydropyrimidine (Formula XI).[13]—The tetrachloro derivative, melting at 127°, is readily hydrolyzed by simply refluxing with water. For example, after boiling 0.0694 g. of the substance for two and one-half hours with 25 cc. of water the solution was titrated with *N* sodium hydroxide and methyl red. The titer was 9.94 cc., corresponding to 0.0363 g. of hydrogen chloride, or 98.9% of the value 0.0367 g. calculated for the liberation of 4 hydrogen chloride. During the refluxing a volatile substance solidified in the condenser tube. This had a strong camphoraceous odor and melted at 44°. It is diethylmalononitrile, the substance described above as a product of the steam distillation of the crude chlorination products. The formation of this nitrile, containing the paired ethyl groupings of the original barbital, establishes the fact that the tetrachloro derivative from which it was obtained also has this structure and that no alkyl migration occurred during the chlorination.

Refluxing with zinc dust and water, however, removed two chlorines and gave a product which was readily isolated by steam distillation. It had a camphoraceous odor, but melted at 117°. This substance is considerably more stable than the tetrachloro derivative. No hydrogen chloride was liberated from it by two and one-half hours' refluxing with water. Like the nitrile, it tends to sublime in the condenser tube. The same product was obtained by reduction of the tetrachloro derivative with zinc dust and alcohol and with zinc dust and acetic acid.

Anal. Calcd. for $C_8H_{12}N_2Cl_2$: N, 13.52; Cl, 34.30. Found: N, 13.40; Cl, 33.78.

When the residue from the distillation was made alkaline with sodium hydroxide and distilled further, the distillate was practically neutral and left no residue on evaporation. No evidence was therefore obtained of a further reduction product.

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[12] Bredt and Iwanoff, Ber., **58**, 56 (1925).

[13] The isomeric formula with both chlorines in the 2-position is less in conformity with the properties of the substance.

The hydrolysis of the tetrachloro derivative into diethylmalononitrile is rather a curious reaction. As already stated, hydrogen chloride is liberated quantitatively. It may be supposed that this hydrolysis results first in the formation of an unstable intermediate product, a 5,5-diethyl-2-keto-4,6-dihydroxydihydropyrimidine (Formula VII), which then breaks up into one molecule each of diethylmalononitrile. water and carbon dioxide. This hypothetical intermediate is simply an enolic tautomer of barbital. No oxygen ethers or other derivatives of it are known. It is possible, however, that the ring breaks open after the first stage of hydrolysis involving only the more reactive chlorines in the 2-position. There would then be formed, by hydrolysis and loss of carbon dioxide, a diimine $Et_2C(CCl{=}NH)_2$ which would promptly lose two molecules of hydrogen chloride and form the dinitrile. The former reaction, where all four chlorines are removed by hydrolysis and an enolic barbital is formed, appeals more strongly to the writer in view of the fact that barbital itself appears to yield small quantities of the nitrile under conditions of simple hydrolysis. In a parallel experiment the same quantity of barbital in the same concentration was refluxed for the same length of time with four equivalents of hydrogen chloride. A very minute quantity of needle-shaped crystals sublimed in the condenser and these had a distinct camphor odor, but the yield was altogether too small for a melting point determination. Here we have the suggestion of an enol–keto equilibrium in the case of barbital.

2,4,6-Triimino-5,5-diethylhexahydropyrimidine (Formula IX).[14]—As was to be expected, the tetrachloro derivative in an inert solvent reacts with dry ammonia. A solution of 1 g. in 50 cc. of absolute alcohol was saturated with dry ammonia, tightly stoppered and allowed to stand at room temperature for several days. In about twenty-four hours a separation of transparent granular crystals began. These continued to grow during the next two days, accompanied by the formation of fern-like crystals of ammonium chloride, until they had attained a diameter of about 5 mm. After filtering and washing with cold water to remove the ammonium chloride the yield was 0.585 g. Evaporation of the mother liquor gave a further yield. The substance is soluble in water and gives a copious precipitate with silver nitrate, hence is the hydrochloric acid salt of a base. It contains alcohol of crystallization, and the transparent crystals effloresce in the oven at 100°. This triimino derivative is rather a strong base since it separates as a mono-hydrochloride salt in the presence of a large excess of ammonia.

Anal. Calcd. for $C_8H_{15}N_5 \cdot HCl$: Cl, 16.32; N, 32.18. Found: Cl, 16.8, 16.2; N, 30.4.

The base has been described[15] as a condensation product of diethylmalononitrile and guanidine. Although the hydrochloric acid salt is moderately stable to dilute acids, the free base is rather easily hydrolyzed. A sample of the hydrochloride salt was treated with the exact equivalent of 0.1 N sodium hydroxide and evaporated on the steam-bath. The odor of ammonia was soon recognized and an insoluble residue was finally obtained which had the properties of diethylmalonylguanidine (Formula X). The 2-imino group is evidently more firmly bound than the 4- and 6-imino groups. Further hydrolysis by dilute sulfuric acid yielded barbital.

Summary

Barbital reacts with phosphorus pentachloride at 115–120° with formation chiefly of diethylcyanoacetyl chloride and 2,2,4,6-tetrachloro-5,5-diethyldihydropyrimidine. The former is a cleavage product of an intermediate partially chlorinated pyrimidine, the reaction being somewhat

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[14] Possibly the tautomeric 4,6-diamino derivative.

[15] German Patent 165,692 (1905).

analogous to the formation of a nitrile acid chloride from camphoric imide, observed by Bredt and Iwanoff. It was identified by conversion into the amide and the free acid.

The tetrachlorodiethyldihydropyrimidine readily undergoes hydrolysis to diethylmalononitrile. It is suggested that this reaction occurs by way of an enolic tautomer of barbital.

Reduction of the tetrachloro derivative with zinc dust yields a stable dichlorodiethyldihydropyrimidine which does not easily undergo further reduction.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

STUDIES IN THE DIPHENYL ETHER SERIES. III. DERIVATIVES OF THE LOCAL ANESTHETIC TYPE[1]

BY C. M. SUTER AND ELMER OBERG

RECEIVED JANUARY 29, 1931 PUBLISHED APRIL 6, 1931

The purpose of this work was to study some derivatives of diphenyl ether which differ from the commonly used esters of *p*-aminobenzoic acid mainly in that the amino and ester groups are not attached to the same benzene ring. By a comparison of the local anesthetic action of these compounds with isomers containing both groups in the same ring it is hoped some conclusions may be drawn concerning the mutual effect of these two atomic complexes. The derivatives here reported upon are esters of 4-(4-aminophenoxy)-benzoic acid.

There are several methods which might be used in synthesizing the 4-(4-nitrophenoxy)-benzoic acid necessary for preparing the desired esters. It has been previously[2] obtained in small amounts by the action of the dipotassium salt of p-hydroxybenzoic acid upon p-chloronitrobenzene. Since the potassium salt of *p*-hydroxybenzaldehyde undergoes this type of reaction very readily, giving an aldehyde which may be oxidized to the desired 4-(4-nitrophenoxy)-benzoic acid, this latter method was used instead of the original one. When this work was practically completed, another feasible method was found in the acetylation of 4-nitrodiphenyl ether and the subsequent oxidation of the 4-(4-nitrophenoxy)-acetophenone.

The 4-(4-nitrophenoxy)-benzoic acid was converted into the acid chloride by the use of thionyl chloride. This was reacted with ethyl, n-butyl and β-diethylaminoethyl alcohols to give the nitro esters, which were catalytically reduced[3] to the desired compounds.

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[1] Presented before the Organic Division of the American Chemical Society at the Cincinnati Meeting, September, 1930.

[2] Haeussermann and Bauer, *Ber.*, 29, 2083 (1896).

[3] Adams, Cohen and Rees, THIS JOURNAL, 49, 1093 (1927).

Preliminary experiments[4] indicate that the ethyl and butyl ester hydrochlorides show a slight local anesthetic action although they are too insoluble in water to be tested adequately. The β-diethylaminoethyl ester monohydrochloride has an activity approximately equal to that of borocaine or procaine, but it is considerably more toxic than these. Although its solubility in water is too small to give the 2% solution generally used, addition of the amount of hydrochloric acid necessary to form the dihydrochloride renders it sufficiently soluble.

Throughout the experimental work, Fischer short-stemmed thermometers were used in obtaining the melting points.

Experimental

4-(4-Nitrophenoxy)-benzaldehyde.—A solution of 45 g. of potassium hydroxide in 25 cc. of hot water was added with stirring to 97 g. of crude p-hydroxybenzaldehyde in 200 cc. of absolute ethyl alcohol. By cooling in ice there was obtained 116 g. or 91% of the theoretical of the potassium salt. The material so obtained was dark red in color but was satisfactory for the following reaction.

To 200 g. (1.27 moles) of *p*-chloronitrobenzene kept at 165–170° was added in small portions with stirring during one hour 93 g. (0.58 mole) of the dry potassium salt. The mixture was then maintained at 190–200° for six hours, cooled and steam distilled to remove the excess *p*-chloronitrobenzene. One crystallization from dilute acetic acid gave 106 g., 75% of the theoretical, of a brownish product which, after treatment with bone-black in alcohol, was obtained as colorless needles melting at 104–105°.

Anal. Calcd. for $C_{13}H_9O_4N$: N, 5.76. Found: N, 5.60, 5.62.

4-(2-Nitrophenoxy)-benzaldehyde.—This was prepared similarly to the preceding by the reaction of the potassium salt of p-hydroxybenzaldehyde with *o*-chloronitrobenzene. It was obtained as a white powder melting at 84–85°.

Anal. Calcd. for $C_{13}H_9O_4N$: N, 5.76. Found: N, 5.90, 5.84.

4-(4-Nitrophenoxy)-acetophenone.[5]—To a solution of 10.8 g. (0.05 mole) of 4-nitrodiphenyl ether and 13.3 g. (0.1 mole) of anhydrous aluminum chloride in 100 cc. of carbon disulfide was added during ten minutes 5 g. (0.06 mole) of acetyl chloride. After refluxing the mixture for fifteen minutes, the solvent was removed by distillation and the residue heated for half an hour longer on the steam-bath. Water was added and the product crystallized from 95% alcohol. The yield was 7 g., 55% of the theoretical, of a colorless product melting at 80–81°.

Anal. Calcd. for $C_{14}H_{11}O_4N$: N, 5.45. Found: N, 5.49, 5.38.

4-(4-Nitrophenoxy)-benzoic Acid.—A mixture of 60 g. of sodium dichromate in 100 cc. of water and 49 g. of the crude aldehyde was warmed until the aldehyde melted; then 43 cc. of concentrated sulfuric acid was added to the stirred mixture during half an hour. After an hour, the mixture was cooled, diluted with water and the insoluble residue extracted several times with hot dilute sodium hydroxide solution. Acidifying this alkaline solution gave 41 g., 79% of the theoretical, of the acid melting at 235–236°. Haeussermann and Bauer[2] report 236–237° for the acid prepared in a different way.

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[4] Our thanks are due Mr. Leonard Fosdick of the Northwestern Dental School for this report.

[5] Dilthey, Bach, Grütering and Hausdorfer, J. prakt. *Chem.*, 117, 361 (1927).

The same acid was obtained in 76% yield by oxidation of **4-(4-nitrophenoxy)**-acetophenone with bleaching powder by warming in water solution. This indicates the structure of this compound to be that assigned to it.

4-(4-Nitrophenoxy)-benzoyl Chloride.—A mixture of 10 g. of the acid and 50 g. of thionyl chloride was refluxed for an hour, the excess thionyl chloride distilled off and the residue extracted several times with petroleum ether (60–90°). There was obtained 9 g., 84% of the theoretical, of a slightly colored product which upon recrystallizing again from the same solvent gave long colorless needles which melted at 79–80'. It is slightly soluble in ether and readily soluble in benzene.

Anal. Calcd. for $C_{13}H_8O_4NCl$: N. 5.04. Found: N, 5.00, 5.05.

The amide was obtained by passing ammonia into a benzene solution of the acid chloride. It melts at 167–168".

Anal. Calcd. for $C_{13}H_{10}O_4N_2$: N, 10.86. Found: N, 10.94, 10.93.

Ethyl **4-(4-Nitrophenoxy)-benzoate.**—A solution of 24 g. of the acid chloride in 125 cc. of absolute ethyl alcohol was warmed on the steam-bath for an hour. Upon cooling, the ester separated as a white powder in nearly quantitative yield. Upon recrystallizing from alcohol, it melted at 74–75°.

Anal. Calcd. for $C_{15}H_{13}O_5N$: N, 4.88. Found: N, 4.74, 4.94.

Ethyl **4-(4-Aminophenoxy)-benzoate.**—A solution of 17.3 g. (0.06 mole) of the nitro ester in 230 cc. of 95% alcohol was reduced with hydrogen in the presence of 0.2 g. of platinum oxide[a] catalyst. Upon removing the solvent, a viscous, slightly colored oil remained which did not crystallize. The hydrochloride was obtained as a white powder by passing hydrogen chloride through a benzene solution of the amine. It had no definite melting point but decomposed at about 165'. It is very slightly soluble in water.

Anal. Calcd. for $C_{15}H_{16}O_3NCl$: N, 4.77. Found: N, 4.76, 4.63.

The acetyl derivative separated from 95% alcohol as colorless crystals melting at 122–123°.

Anal. Calcd. for $C_{17}H_{17}O_4N$: N, 4.68. Found: N, 4.70, 4.53.

Butyl 4-(4-Nitrophenoxy)-benzoate.—This was obtained from **4-(4-nitrophenoxy)-benzoyl** chloride and n-butyl alcohol as a thick yellow oil which distilled at 250–255' at 5 mm.

Anal. Calcd. for $C_{17}H_{17}O_5N$: N, 4.44. Found: N, 4.50, 4.58.

Butyl **4-(4-Aminophenoxy)-benzoate.**—This was obtained similarly to the ethyl homolog by reduction of the nitro ester. It was obtained as a jelly-like material which did not crystallize. It was converted into the hydrochloride, which is practically insoluble in water and upon heating decomposes at 155–160°.

Anal. Calcd. for $C_{17}H_{20}O_3NCl$: N, 4.35. Found: N, 4.35, 4.38.

The acetyl derivative separated from 95% alcohol as a white flocculent material which melted at 98–99'.

Anal. Calcd. for $C_{19}H_{21}O_4N$: N, 4.29. Found: N, 4.33, 4.41.

β-Diethylaminoethyl 4-(4-Nitrophenoxy)-benzoate Hydrochloride.—A solution of 17 g. of the acid chloride in 100 cc. of benzene was treated with 6 g. (0.05 mole) of β-diethylaminoethyl alcohol in 15 cc. of benzene. The mixture was heated on the steam-bath for an hour, cooled and filtered. There was obtained 18 g. or 90% of the theoretical of material which decomposed at 100–110'.

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[6] Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

Anal. Calcd. for $C_{19}H_{23}O_5N_2Cl$: N, 7.00. Found: N, 7.05, 7.08.

β-Diethylaminoethyl 4-(4-Aminophenoxy)-benzoate Hydrochloride.—This was obtained, by reduction of the nitro compound described in the preceding preparation, as a jelly-like material which is insoluble in ether and benzene, but dissolves in warm water and separates upon cooling in an amorphous condition.

Anal. Calcd. for $C_{19}H_{25}O_3N_2Cl$: N, 7.68. Found: N, 7.33, 7.36.

Summary

A number of local anesthetic type derivatives of diphenyl ether have been prepared in which the carboxy and amino groups are not attached to the same benzene ring.

Although these derivatives show considerable anesthetic action, they are too toxic to be of practical value.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE OXIMES OF ORTHO HYDROXY BENZOPHENONE

BY E. P. KOHLER AND W. F. BRUCE

RECEIVED JANUARY 30, 1931 PUBLISHED APRIL 6, 1931

The oximes of o-hydroxy benzophenone have acquired a certain importance in connection with the interpretation of the Beckmann rearrangement. One of the two possible oximes was first made by Cohn,[1] who described a product melting at 134°. Meisenheimer and Meis[2] recently repeated the work under somewhat different conditions, but likewise obtained only a single oxime (135°). Like o-chloro benzophenone and o-bromo benzophenone, therefore, o-hydroxy benzophenone appeared to be capable of forming but one oxime that was sufficiently stable for isolation, and it seemed probable that the known oximes of these three ketones-had the same configuration.

Since alkalies convert the known oximes of o-chloro and o-bromo benzophenone into a cyclicc ompound—phenyl indoxazene—Meisenheimer and Meis concluded that these were probably *syn* oximes. They subsequently verified[3] this conclusion beyond all doubt by preparing the much more reactive dinitro o-chloro benzophenone oxime and showing that it forms the corresponding indoxazene under conditions under which isomerization of the oxime need not be feared. The configuration of these three oximes can therefore be regarded as established by their relation to cyclic compounds. When they were subjected to a Beckmann rearrangement, all three gave products which were in accord with Meisenheimer's interpretation of this rearrangement.

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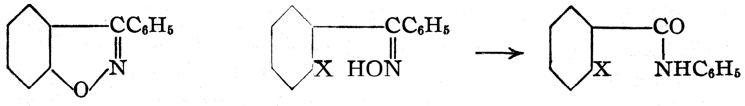
[1] Cohn, Monatsh., 17, 102 (1896).

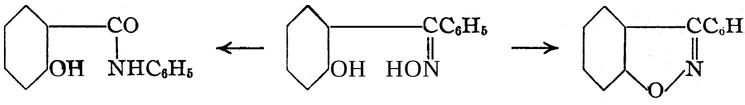
[2] Meisenheimer and Meis, Ber., 57, 289 (1924).

[3] Meisenheimer, Zimmermann and v. Kummer, Ann., 446, 208 (1926).



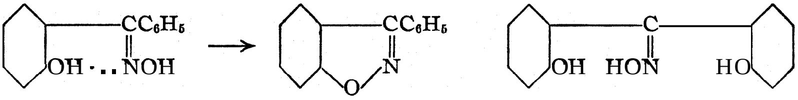
II I III

By analogy with these halogen compounds, the known oxime of o-hydroxy benzophenone would be expected to yield salicylanilide on rearrangement and phenyl indoxazene on dehydration. Meisenheimer and Meis found that it is readily rearranged by phosphorus pentachloride and that the principal product is salicylanilide, but they also found that it resisted all their efforts to convert it into the cyclic compound.



IV V II

In order to account for this unexpected resistance to dehydration, they resorted to the same auxiliary hypothesis that Meisenheimer had adopted to explain why the y-dioxime of benzil, which according to Meisenheimer's interpretation is the *amphi* form, loses water more readily than any of its isomers.[4] Accordingly, they assumed that for the elimination of water, the interplay of residual valences was decisive, and they predicted that the indoxazene derivative would be readily formed from the *anti* form.



VI II VII

This prediction lost much of its probability when Auwers and Jordan[5] showed that it was impossible to transform the oxime of *o,o'*-dihydroxy benzophenone (VII) into an indoxazene derivative. As a matter of fact the prediction is wrong; we have prepared both of the oximes of o-hydroxy benzophenone, and have found that neither of them can be dehydrated. It is impossible, therefore, to establish the configuration of these oximes by relating them to phenyl indoxazene.

Surprisingly enough, in view of the fact that isomeric oximes of ortho substituted benzophenones have so seldom been obtained,[6] both of the oximes of o-hydroxy benzophenone are relatively stable substances. They differ little in solubility and melting point but they are readily distinguished by their crystalline form, the h-oxime (143°) crystallizing from benzene

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[4] Meisenheimer and Lamparter, *Ber.*, 57, 276 (1924).

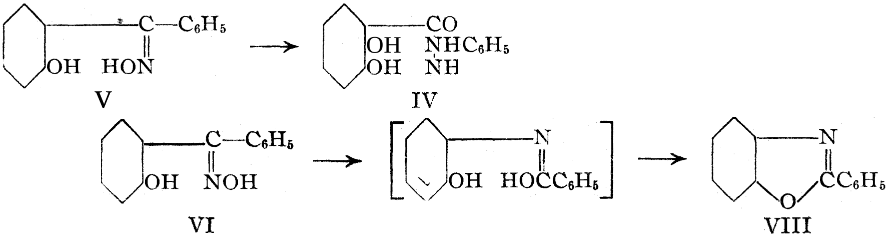
[5] Auwers and Jordan, *ibid.*, 58, 26 (1925).

[6] *(a)* A. W. Smith, *ibid.*, 24,4057 (1891); (b) A. Hantzsch, *ibid.*, 25,2164 (1892); (c) Auwers and Myenburg, *ibid.*, 24, 2383 (1891); 29, 1264 (1896); (d) Auwers and Jordan, *ibid.*, 57, 800 (1924).

in plates while the n form (141°) appears in needles. Neither passes into the other in boiling solvents or at the melting point. At higher temperatures the h-form sublimes unchanged, while the n-form is changed to its isomer, but even at 185–200° the process is exceedingly slow.

Although both oximes can be obtained in alkaline solutions of hydroxylamine, and Cohn, as well as Meisenheirner and Meis, doubtless had mixtures of the two, the needles must be regarded as the "alkali-stable" form because boiling alkalies slowly convert the plates into this form, Formic acid, on the other hand, changes the n- to the h-form; this may, therefore, be regarded as the "acid-stable" oxime, but the term is misleading because formic acid also very readily brings about a Beckmann rearrangement.

With phosphorus pentachloride in ether each oxime yields a single rearrangement product, the n-oxime being converted into salicylanilide and the h-oxime into 2-phenyl benzoxazole (VIII). As usual the process is accompanied by side reactions but no salicylanilide is formed from the h-oxime and no phenyl benzoxazole from the isomer. Since Meisenheimer's interpretation of the Beckmann rearrangement has proved to be correct in every case in which an oxime has been obtained from a cyclic compound, we regard the n-form as the syn and the h-form as the *anti* oxime.



From the foregoing account it is evident that the isomeric oximes of o-hydroxy benzophenone do not furnish any independent evidence with respect to the proper interpretation of the Beckmann rearrangement. Their behavior, however, serves to dispel some of the doubts raised by Auwers and Seyfried[7] concerning the use of this rearrangement for determining configurations. These authors point out that not infrequently a single oxime gives two rearrangement products and that while, as is generally assumed, these products may be due to isomerization of part of the oxime, antecedent to rearrangement, this is not certain because they may also be due to different modes of rearrangement of the same oxime. In the absence of evidence to the contrary, this is doubtless true. We have found, however, that in the case of the n-oxime, which is exceedingly sensitive to acids, it is possible to get a single rearrangement product by operating with phosphorus pentachloride in absolute ether, at a low temperature; and we also found that while formic acid very readily transforms this oxime into the

[7] Auwers and Seyfried. Ann., 484, 178 (1930).

rearrangement product of its isomer, it is possible to isolate the h-oxime as an intermediate in the process. We therefore believe that even when but one isomer is known, the Beckmann rearrangement is useful if it is employed with sufficient care.

Experimental Part

Both of the oximes of o-hydroxy benzophenone can be obtained directly from the ketone by treating it with hydroxylamine in an alkaline medium. The result of this treatment depends mainly, at any rate, upon the temperature. At the ordinary temperature the product is almost pure *h*-**oxime,** which crystallizes in plates. In boiling solutions the product is a mixture in which the quantity of n-oxime increases with the time that the solution is boiled. From mixtures which are composed mainly of either isomer it is comparatively easy to get pure substances by recrystallization from benzene and petroleum ether, but it is not feasible to separate mixtures containing considerable quantities of both components in this manner.

The h-oxime is most readily obtained by operating at the ordinary temperature. Thus 0.5 g. of the ketone was added to 4 cc. of 40% aqueous potassium hydroxide. The ketone dissolved with the characteristic yellow coloration and a yellow solid soon precipitated from the solution. To this mixture was added 0.5 g. of hydroxylamine hydrochloride. The temperature rose, the yellow solid soon dissolved and the intense yellow color disappeared within fifteen minutes. The solution was then acidified with hydrochloric acid; it deposited a white precipitate which was collected on a funnel, washed with a little 50% methyl alcohol and dried. The crude product weighed 0.45 g. and melted at 128–130°. Recrystallization from benzene and a little petroleum ether gave 0.35 g. of pure oxime, crystallizing in thin plates and melting at 142–143°. The pure oxime crystallizes well from dilute methyl alcohol in large thick plates but it is very difficult to separate a mixture of the oximes by crystallization from this solvent.

Anal. Calcd. for $C_{13}H_{11}O_2N$: C, 73.2; H, 5.1. Found: C, 72.9; H, 5.2.

The *n-oxime* is probably obtained most readily by heating the h-oxime with strong alkalies. Thus a solution of 0.5 g. of the h-oxime in 20 cc. of 20% aqueous sodium hydroxide was boiled vigorously for two hours, during which it became slightly yellow (possibly because some of the hydroxy ketone was regenerated). On acidification the solution deposited a solid contaminated with a small quantity of red oil. Recrystallization from benzene and petroleum ether yielded 0.3 g. of a pure product crystallizing in needles and melting at 141–142°. A mixture of the two forms melted at 115–120°.

Anal. Calcd. for $C_{13}H_{11}O_2N$: C, 73.2; H, 5.1; N, 6.6. Found: C, 73.5; H, 5.4; N, 7.0.

Separation of Mixtures.—To a solution of 5 g. of o-hydroxy benzophenone and 5 g. of hydroxylamine hydrochloride in 50 cc. of methyl alcohol was added a solution of 8 g. of potassium hydroxide in 8 cc. of water. The mixture was boiled for two hours, then poured into 150 cc. of water. A slight gummy precipitate was removed by filtration, and then the clear filtrate was partially neutralized with 3 cc. of glacial acetic acid; it deposited 1.34 g. of a colorless solid which was collected on a filter, washed and dried. One recrystallization of this first crop from 4 cc. of benzene gave the pure h-oxime melting at 143°.

From the filtrate from the first fraction 1 cc. of glacial acetic acid precipitated 1.08 g. of a pale yellow solid which melted at 128–135° and which proved to be a mixture of the two isomers, separable most readily by a repetition of the operation. Final acidification with 3 cc. of glacial acetic and 3 cc. of concentrated hydrochloric acids resulted in

0.8 g. of a colorless precipitate which after one recrystallization from benzene and petroleum ether was pure n-oxime.

The Action of Alkalies on the **Oximes.—It** has been shown that the isomerization of the h-oxime by alkalies is accompanied by secondary reactions that lead to the development of color. The n-oxime appears to be much more stable in boiling alkalies, for when a solution of **0.5** g. of the substance in **20** cc. of **20%** aqueous sodium hydroxide was boiled for two hours it remained colorless and **0.45** g. of the pure oxime was recovered when the solution was acidified.

The Action of Heat on the **Oximes.—A small** quantity (**0.24** g.) of the h-oxime was heated under **25** mm. to 175–180° for half an hour during which most of it (0.15 g.) sublimed to the upper part of the flask. The sublimate was unchanged oxime. The residue was dissolved in a little methyl alcohol in which the dehydration product, phenyl indoxazene, is sparingly soluble, but nothing except unchanged h-oxime could be detected in the solution. Two-tenths of a gram of the n-oxime was heated in a similar manner to 180–200° and a part of the material sublimed in plates. Solid residue and sublimate dissolved completely in **2** cc. of methyl alcohol and inoculation of this solution with phenyl indoxazene had no effect. The solution, on cautious dilution with water, deposited **0.15** g. of the h-oxime, and further dilution gave **0.05** g. more or less pure material (137–140°). At elevated temperatures, therefore, the n-oxime does not undergo dehydration but is changed to the k-isomer.

The Action of Phosphorus Pentachloride on the **Oximes.—To** a solution of **1** g. of the n-oxime in **30** cc. of absolute ether was added **1.9** g. of phosphorus pentachloride. The cloudy solution was allowed to remain at 20° for fifteen minutes, then mixed with **20** g. of ice. The ethereal layer was washed with hydrochloric acid and with water, dried and evaporated. It left a gummy residue which was completely soluble in alkalies, therefore contained no phenyl benzoxazole. From the alkaline solution carbon dioxide precipitated **0.45** g. of salicylanilide melting at **132–133°.**

In a similar manner **1** g. of the h-oxime was treated with **1.5** g. of phosphorus pentachloride. The washed and dried ethereal solution on evaporation left a gummy residue of which all but **0.42** g. was soluble in alkali. The insoluble portion was identified as 2-phenyl benzoxazole melting at 102–103°. From the alkaline solution carbon dioxide precipitated a solid which after recrystallization melted at 164–167°. Only a small amount of this substance was obtained in fairly pure state; it had the properties of *o*-aminophenol, a cleavage product of the compound resulting from the initial rearrangement.

The Action of Hydrogen Chloride on the **Oximes.—Attempts** to dehydrate one or other of the oximes with dry hydrogen chloride met with no success. From ethereal solutions of h-oxime dry hydrogen chloride precipitated a yellow hydrochloride that melted at **118–120°** when freshly prepared but which rapidly deteriorated when kept in a vacuum desiccator. When an alcoholic solution of this chloride was immediately diluted with water, the h-form was recovered, practically quantitatively, and when the chloride was dissolved in chloroform, hydrogen chloride was given off and again the h-form was recovered. But when the chloride was heated to 140–145° it decomposed freely, and moisture condensed on the cool part of the tube. From the residue alkali extracted *o*-hydroxy benzophenone and left 2-phenyl benzoxazole, which was identified by a mixed melting point.

The n-form likewise gave a solid hydrochloride. This melted at **132–134'** and regenerated the n-oxime when it was dissolved in hot chloroform or when its solution in alcohol was diluted with water. When it was heated to **145°** this oxime likewise gave 2-phenyl benzoxazole. Under these conditions, therefore, neither of the oximes can be dehydrated.

The Action of Formic Acid on the Oximes.—Preliminary experiments showed that neither cold concentrated sulfuric nor glacial acetic acid has any action on the oximes. We therefore turned to formic acid, which is known[6d] to be much more effective. Both oximes gave, along with a small quantity of yellow oil which was doubtless the hydroxy ketone due to hydrolysis, mainly phenyl benzoxazole. This result was to be expected in the case of the h-oxime because the oxazole derivative is obtained from the normal Reckmann rearrangement product of this oxime. But in the case of the n-oxime the formation of this product involves either an abnormal rearrangement or a combination of isomerization and rearrangement.

In order to decide between these alternatives we repeated the experiment with the n-oxime with much greater care. To this end a solution of 0.25 g. of the oxime in 2 cc. of formic acid (sp. gr. 1.20) was heated without delay to 100° for five minutes. The yellow solution was then cooled and diluted with 10 cc. of water. A gummy yellow precipitate separated. Excess of sodium carbonate was added and the mixture was left to itself for several hours, during which the precipitate became solid and nearly white. It was collected on a sintered glass filter and digested for fifteen to twenty minutes with sodium bicarbonate solution. After this had been sucked off, a clean receiver was placed under the filter and the solid was stirred with 5 cc. of 10% sodium hydroxide. A partial solution occurred. The insoluble part was washed with alkali, water and dilute methyl alcohol (about 50%), and dried. It weighed 0.05 g. and melted at 97–100°. The mixed melting point with 2-phenyl benzoxazole gave no depression.

To the faintly turbid alkaline filtrate was added drop by drop with shaking 5% acetic acid until a more pronounced permanent turbidity just became evident. The solution stood overnight and the small brown plates which formed were filtered off. They weighed 0.04 g. and melted at 134–137°. On crystallization from benzene and petroleum ether a solid melting at 140–141° was secured. The mixed melting point with the plate form oxime was 141–143°, and with the needle form 110–115°. It is important not to add more than the specified amount of acid in precipitating this portion since a slight excess will precipitate the n-form also, and separation of a mixture of the isomers by crystallization is practically impossible unless one form is very largely in excess.

Acidification of the faintly alkaline filtrate gave 0.12 g. of white unchanged *n*-oxime melting at 138–140°, mixed melting point with the original n-oxime, 139–141° This procedure was carried out twice with the same result.

Summary

The stereoisomeric oximes of o-hydroxy benzophenone have been prepared. Neither of them can be dehydrated to a cyclic compound. Their behavior, therefore, contributes no independent evidence with respect to the proper interpretation of the Beckmann rearrangement, but indicates that this rearrangement is reliable when it is employed with sufficient care.

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

STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. THE PREPARATION AND RESOLUTION OF 3,5,3′,5′-TETRAMETHYL-2,2′-DIFLUORO-6,6′-DIAMINODIPHENYL. XIV[1]

BY E. C. KLEIDERER[2] AND ROGER ADAMS

RECEIVED FEBRUARY 2, 1931 PUBLISHED APRIL 6, 1931

The interpretation of the degree of resistance to free rotation of the rings in 2,2′,6,6′-substituted diphenyls through x-ray values representing the size of the groups, was discussed in detail in an earlier paper.[3] Since that time these values have been applied to various new diphenyl compounds and have fitted in better with the experimental facts than might have been anticipated. However, sufficient data have not as yet been collected so that generalizations might be drawn which would make possible the prediction of the properties of any new derivatives in a quantitative way.

It was pointed out that any diphenyl molecule which showed interference between the 2,2′ and 6,6′ substituting groups of only a few hundredths of an Å. would probably racemize readily, a property not shown by most of the molecules studied up to this time. It may thus be seen that in 2,2′-difluoro-6,6′-diaminodiphenyl such conditions should exist. On each side of the molecule the interference would be only 0.05 Å.: C–F, 1.39 Å. + C–NH_2, 1.56 Å. = 2.95Å. – 2.90Å. (vertical distance between the 2,2′ carbon atoms) = 0.05 Å. In this investigation a homolog of this compound has been described and its ease of racemization determined. The properties are exactly those which were predicted.

The compound synthesized was 3,5,3′,5′-tetramethyl-2,2′-difluoro-6,6′-diaminodiphenyl (V). It was readily resolved through the dicamphorsulfonate salt. The active amines had surprisingly low rotations compared to most of the other optically active diphenyls previously studied; $[\alpha]^{20}_{D}$ $-4.1°$ and $[\alpha]^{20}_{D}$ $+3.2°$. The former undoubtedly is the maximum rotation for the active compound as it was obtained from the pure, less soluble salt.

The active forms racemized with the greatest ease. By boiling in ethyl alcohol, the I-form was half racemized in one hour and completely racemized in two hours; in glacial acetic acid it was entirely racemized in half an hour; even in boiling methyl alcohol the racemization was complete in four hours.

To synthesize this compound the following series of reactions was carried out: 3,5-dimethyl-2-aminobenzene ⟶ 3,5-dimethyl-2-amino-6-nitro-

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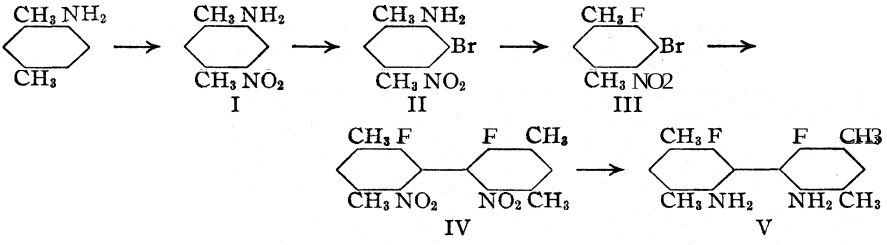
[1] For the preceding papers in this series see Browning and Adams, THIS JOURNAL. 52, 4098 (1930); Stanley and Adams, 52, 4471 (1930); Steele and Adams, 52, 4528 (1930); Shildneck and Adams, 53, 343 (1931); Bock and Adams, 53,374 (1931).

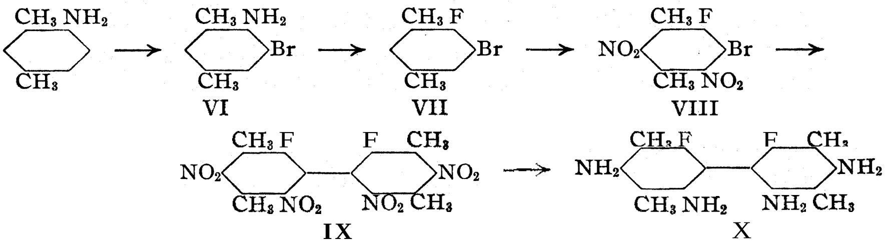
[2] This communication is a portion of a thesis submitted by E. C. Kleiderer in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Stanley and Adams, THIS JOURNAL, 52,1200 (1930).

benzene (I) → 3,5-dimethyl-2-amino-6-nitro-1-bromobenzene (II) → 3,5-dimethyl-2-fluoro-6-nitro-1-bromobenzene (111) → 3,5,3′,5′-tetramethyl-2,2′-difluoro-6,6′-dinitrodiphenyl (IV) → 3,5,3′,5′-tetramethyl-2,2′-difluoro-6,6′-diaminodiphenyl (V).



In the experimental part is also described the preparation of 3,5,3′,5′-tetramethyl-2,2′-difluoro-4,4′,6,6′-tetraaminodiphenyl, as follows: 3,5-dimethyl-2-aminobenzene → 3,5-dimethyl-2-amino-1-bromobenzene (VI) → 3,5-dimethyl-2-fluoro-1-bromobenzene (VII) → 3,5-dimethyl-2-fluoro-4,6-dinitro-1-bromobenzene (VIII) → 3,5,3′,5′-tetramethyl-2,2′-difluoro-4,6,4′,6′-tetranitrodiphenyl (IX) → 3,5,3′,5′-tetramethyl-2,2′-difluoro-4,6,4′,6′-tetraaminodiphenyl (X).



This compound was synthesized before the corresponding diamino derivative but, in attempting resolution, crystalline salts could not be isolated using d-tartaric acid, d-camphorsulfonic acid, or *d*-bromocamphorsulfonic acid.

Experimental

3,5-Dimethyl-2-amino-6-nitrobenzene (I).—In a 600-cc. beaker, 20 g. of *m*-xylidine was dissolved in 200 g. of concentrated sulfuric acid. The mixture was then cooled to 5° and not allowed to rise above 15°. To this was slowly added with stirring 16.5 g. of concentrated nitric acid (sp. gr. 1.42). After all of the nitric acid had been added, the mixture was stirred for thirty minutes longer. It was then poured onto ice, when the amine sulfate precipitated. This was filtered off and made alkaline with 10% sodium carbonate solution. The free amine was purified by crystallization from 50% alcohol–water mixture. A small amount of an insoluble by-product always resulted which may have been a dinitro compound. The mononitro compound formed deep orange needles melting at 123–124° and the yield was 23 g. (84%).

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[4] Noelting and Collin, *Ber.*, 17, 265 (1884).

3,5-Dimethyl-2-amino-6-nitro-1-bromobenzene (II).[5]—In a 1-liter round-bottomed flask, 10 g. of 3,5-dimethyl-2-amino-6-nitrobenzene was dissolved in 100 g. of glacial acetic acid. To this was added, with stirring, 9.5 g. of bromine dissolved in 50 cc. of glacial acetic acid. During the addition, the hydrobromide of the brominated amine crystallized out in white needles. The crystals were filtered off and made alkaline with a 10% sodium carbonate solution and the base thus obtained was used directly for further experimentation.

3,5-Dimethyl-6-nitro-1-bromobenzene-2-diazoniumborofluoride.—In a 300-cc. beaker was placed 25 cc. of concentrated hydrochloric acid. In this was suspended 10 g. of 3,5-dimethyl-2-amino-6-nitro-1-bromobenzene, and the mixture cooled to 0°. A solution of saturated sodium nitrite was added until there remained a slight excess of free nitrous acid as determined by potassium iodide–starch test papers. The solution was filtered from any sodium chloride and to the filtrate was added 27.6 g. of a solution of hydroborofluoric acid, made by mixing 20 g. of 48% hydrofluoric acid and 7.6 g. of boric acid. Upon the addition of the acid, the borofluoride precipitated in white needles. It was filtered off and washed with more hydroborofluoric acid. The yield was 9 g. (67%). The decomposition point of the compound was 195°.

3,5-Dimethyl-2-fluoro-6-nitro-1-bromobenzene (III).—In a small Pyrex test-tube, connected by a wide glass delivery tube to a 500-cc. distilling flask cooled in ice, was placed 3 g. of the 3,5-dimethyl-6-nitro-1-bromobenzene-2-diazoniumborofluoride. The compound was heated with a Méker burner and as soon as it commenced to decompose, the system was placed under reduced pressure and heating continued. The compound became very black and charred but a quantity of the fluorine derivative distilled over. Heating was continued until no more material could be distilled, when the test-tube was emptied of the carbon and refilled with 3 g. more of the borofluoride. It was found that the yield increased when small quantities of the borofluoride were decomposed at a time. Additional fluorine compound could be obtained by reheating the carbon residue obtained from previous decompositions. The fluorine compound was purified by mixing with water and steam distilling and then crystallizing from low-boiling petroleum ether. It formed yellow needles, melting at 49–51". The yield was 17 g. from 50 g. of borofluoride (45%).

Anal. Calcd. for $C_8H_7O_2BrFN$: Br, 32.22. Found: Br, 31.85.

3,5,3′,5′-Tetramethyl-2,2′-difluoro-6,6′-dinitrodiphenyl (IV).—In a 200-cc., round-bottomed, 3-necked flask containing a stirrer and an air-cooled reflux condenser were placed 10 g. of 3,5-dimethyl-2-fluoro-6-nitro-1-bromobenzene and 20 cc. of dry nitrobenzene. The flask was heated in a metal bath for five hours to 200° and vigorously stirred. During this time 20 g. of powdered copper bronze was added in small amounts. The mixture was filtered and the solid was washed with acetone. The filtrates were steam distilled and the diphenyl compound remained as a residue. This was washed with alcohol to remove any remaining nitrobenzene and was crystallized from 50% acetone–water mixture. The compound formed white plates melting at 234–236° (corr.). The yield was 5 g. (75%).

Anal. Calcd. for $C_{16}H_{14}O_4F_2N_2$: N, 8.33. Found: Kjeldahl ($TiCl_3$), N, 8.48.

3,5,3′,5′-Tetramethyl-2,2′-difluoro-6,6′-diaminodiphenyl (V).—In a 400-cc. beaker was placed 200 cc. of glacial acetic acid, 20 cc. of concentrated hydrochloric acid and 8 g. of 3,5,3′,5′-tetramethyl-2,2′-difluoro-6,6′-dinitrodiphenyl. This mixture was heated to boiling and to it was added 6 g. of zinc dust. The reduction was allowed to proceed at the boiling point for ten minutes. The mixture was then made alkaline by pouring it into an ice-cold solution of 10% sodium hydroxide. The diamine was filtered off

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[5] Noelting, Braun and Thesmar, *Ber.*, 34, 2257 (1901).

and recrystallized from a 50% alcohol–water mixture. It formed fine white needles, melting at 154–155° (corr.). The yield was 4.5 g. (68%).

Anal. Calcd. for $C_{16}H_{18}F_2N_2$: N, 10.14. Found: N, 9.88.

Resolution of **3,5,3′,5′-Tetramethyl-2,2′-difluoro-6,6′-diaminodiphenyl.**—To a solution of 8.6 g. of the diamine in 130 cc. of anhydrous ethyl acetate was added 15 g. of d-camphorsulfonic acid dissolved in 200 cc. of anhydrous ethyl acetate. The solution was boiled for several minutes, when the salt precipitated out. After cooling and filtering the salt, it was found that all but 2.5 g. of the salt had precipitated. The salt was dissolved in a mixture of 170 cc. of anhydrous ethyl acetate and 28 cc. of absolute ethyl alcohol by heating and the solution was then allowed to stand for six hours. At the end of this time 7 g. of crystals had separated, which were filtered off and washed with anhydrous ethyl acetate and dried. This was shown to be essentially pure I-salt by comparison of the rotation with that of recrystallized material, m. p. 171–173°.

Rotation. 0.1500 g. made up to 15 cc. with absolute alcohol at 20° gave α_D \$0.52"; 1 = 2; $[\alpha]^{20}_{D}$ +26.0°. Recrystallizing from 100 cc. of anhydrous ethyl acetate and 20 cc. of absolute alcohol gave 5 g. of crystals.

Rotation. 0.1500 g. made up to 15 cc. with absolute alcohol at 20° gave α_D +0.52°; l = 2, $[\alpha]^{20}_{D}$ +26.0°.

Anal. Calcd. for $C_{16}H_{18}F_2N_2 \cdot 2C_{10}H_{15}O(SO_3H)$: S, 8.65. Found: S, 8.40.

The mother liquor from the first crop of crystals was evaporated to 125 cc., 50 cc. more of anhydrous ethyl acetate was added, and the solution allowed to stand overnight at room temperature. A crop of 6.7 g. of crystals came down which consisted of a mixture of the less and more soluble salts. The mother liquor from the second crop of crystals was evaporated to 75 cc. and 75 cc. more of anhydrous ethyl acetate was added. On standing overnight, a crop of 4.5 g. of crystals came down which was filtered off and washed with a small amount of anhydrous ethyl acetate, m. p. 125–130°.

Rotation. 0.1500 g. made up to 15 cc. with absolute alcohol at 20° gave α_D +0.60°; l = 2, $[\alpha]^{20}_{D}$ 30.0°. The salt was recrystallized from 100 cc. of anhydrous ethyl acetate.

Rotation. 0.1500 g. made up to 15 cc. with absolute alcohol at 20° gave a, \$0.65"; 1 = 2, $[\alpha]^{20}_{D}$ +32.5°. The salt was again recrystallized from anhydrous ethyl acetate.

Rotation. 0.1500 g. made up to 15 cc. with absolute ethyl alcohol at 20° gave α_D \$0.65"; *1* = 2, $[\alpha]^{20}_{D}$ \$32.5'.

Anal. Calcd. for $C_{16}H_{15}F_2N_2 \cdot 2C_{10}H_{15}O(SO_3H)$: S, 8.65. Found: S, 8.45.

***l*-3,5,3′,5′-Tetramethyl-2,2′-difluoro-6,6′-diaminodiphenyl.**—To the less soluble salt dissolved in water at 0° was added a solution of 10% sodium carbonate. The active amine, which separated in fine white needles, melted at 150–152° (corr.).

Rotation. 0.4352 g. made up to 15 cc. in acetone at 20° gave a, –0.24"; l = 2, $[\alpha]^{20}_{D}$ –4.1".

It was recrystallized from 50% acetone–water mixture by dissolving in cold solvent and evaporating, with stirring, under diminished pressure in the cold until the amine just commenced to crystallize. The melting point was 151–152" (corr.).

Rotation. 0.4000 g. made up to 15 cc. in acetone at 20° gave a, –0.22'; 1 = 2, $[\alpha]^{20}_{D}$ –4.1°.

Anal. Calcd. for $C_{16}H_{18}F_2N_2$: N, 10.14. Found: N, 10.49.

***d*-3,5,3′,5′-Tetramethyl-2,2′-difluoro-6,6′-diaminodiphenyl.**—The d-form was obtained in a manner similar to the 1-form and melted as obtained directly from the salt at 150–151" (corr.).

Rotation. 0.4000 g. made up to 15 cc. in acetone at 20° gave a, +0.16°; *1* = 2, $[\alpha]^{20}_{D}$ +3.0°. The active amine was recrystallized using the procedure for the ***l*-form** and melted at 150–151° (corr.).

Rotation. 0.4000 g. made up to 15 cc. in acetone at 20° gave a, +0.17°; l = 2, $[\alpha]^{20}_{D}$ + 3.2'. Another crystallization gave no change in rotation.

Anal. Calcd. for $C_{16}H_{18}F_2N_2$: N, 10.14. Found: N, 10.60.

Racemization Experiments

1. The rotation was taken on the *l*-amine in absolute alcohol.

Rotation. 0.4000 g. made up to 15 cc. with absolute alcohol at 20° gave a, −0.21°; l = 2, $[\alpha]^{20}_{D}$ −4.0°. The solution was refluxed for thirty minutes and the rotation taken; it was found to be $[\alpha]^{20}_{D}$ −1.5'; after one hour $[a]^{20}_{D}$ −1.4° and at the end of two hours $[\alpha]^{20}_{D}$ 0°.

2. The rotation was taken on the 1-amine in glacial acetic acid.

Rotation. 0.2000 g. made up to 15 cc. with glacial acetic acid at 20° gave a, −0.16°; I = 2, $[\alpha]^{20}_{D}$ −6.0'. After refluxing for fifteen minutes, the rotation was $[\alpha]^{20}_{D}$ −2.6° and in thirty minutes, $[\alpha]^{20}_{D}$ 0°.

3. The rotation was taken on the 1-amine in methyl alcohol

Rotation. 0.4000 g. made up to 15 cc. with methyl alcohol at 20° gave a,, −0.22°; l = 2, $[\alpha]^{20}_{D}$ −4.1°. After refluxing, the following readings were obtained: one hour, $[\alpha]^{20}_{D}$ −2.5°; two hours, $[\alpha]^{20}_{D}$ −1.7'; three hours, $[\alpha]^{20}_{D}$ −0.09'; four hours, $[\alpha]^{20}_{D}$ −0.0'.

3,5-Dimethyl-1-bromobenzene-2-diazoniumborofluoride.—In a 300-cc. beaker was placed 20 cc. of concentrated hydrochloric acid. In this was suspended 5 g. of 3,5-dimethyl-2-amino-1-bromobenzene[6] and the mixture cooled to 0°. The amine was diazotized by addition of a saturated solution of sodium nitrite in slight excess as shown by potassium iodide starch test papers. The diazonium solution was filtered from any sodium chloride and to the filtrate was added 27.6 g. of a solution of hydroborofluoric acid, made by mixing 20 g. of 48% hydrofluoric acid and 7.6 g. of boric acid. Upon addition of the acid, the borofluoride precipitated in white needles. These were filtered off and washed with more hydroborofluoric acid. The yield was 4.5 g. (60%). The decomposition point was 161°.

3,5-Dimethyl-2-fluoro-1-bromobenzene (VII).—A quantity of diazonium borofluoride was placed in a 500-cc. distilling flask set for distillation. The flask was placed in a metal bath and heated to 170°, when decomposition occurred. The borontrifluoride was run through a dilute solution of sodium hydroxide. Water was added to the heated product and the fluorine derivative steam distilled. The yield was quantitative. The 3,5-dimethyl-2-fluoro-1-bromobenzene was purified by distillation: b. p. 87–89" at 11 mm., n^{20}_{D} 1.3100, d^{20}_{20} 1.452.

Anal. Calcd. for C_8H_8BrF: Br, 39.40. Found: Br, 39.85.

3,5-Dimethyl-2-fluoro-4,6-dinitro-1-bromobenzene (VIII).—In a cooled 100-cc. beaker was placed 25 cc. of cold fuming nitric acid (sp. gr. 1.60), and the mixture cooled to 0°. To this was added slowly 3.6 g. of 3,5-dimethyl-2-fluoro-1-bromobenzene. The mixture was allowed to stand for three minutes and was then poured onto ice. A very light yellow substance precipitated, which on purification from 70% alcohol–water mixture melted at 86–87°. The yield was 4.6 g. (88%).

Anal. Calcd. for $C_8H_6O_4BrFN_2$: Br, 27.30. Found: Br, 27.27.

3,5,3',5'-Tetramethyl-2,2'-difluoro-4,6,4',6'-tetranitrodiphenyl (IX).—In a 200-cc. 3-necked, round-bottomed flask, containing a stirrer and a reflux air condenser, was placed 30 cc. of dry nitrobenzene The flask was heated for five hours to 190°, and the contents vigorously stirred. During this time 10 g. of 3,5-dimethyl-2-fluoro-4,6-

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[6] Wheeler and Thomas, THIS JOURNAL, **50**, 2286 (1928). See also Schiemann, Ber., **60**, 1186 (1927).

dinitro-1-bromobenzene and 10 g. of powdered copper bronze were added in small portions. The mixture was then filtered and the solid washed with acetone. The filtrate was steam distilled and the diphenyl compound was left as a residue. This was washed with alcohol to remove the remaining traces of nitrobenzene and was recrystallized from a 50% acetone–water mixture. It formed long white needles melting at 202–204° (corr.). The yield was 5 g. (69%).

Anal. Calcd. for $C_{16}H_{12}O_8F_2N_4$: N, 13.13. Found: Kjeldahl ($TiCl_3$), N, 12.90.

3,5,3′,5′-Tetramethyl-2,2′-difluoro-4,6,4′,6′-tetraaminodiphenyl (X).—In a 200-cc. beaker, 3.8 g. of the tetranitro compound was dissolved in 30 cc. of boiling acetic acid and 5 cc. of concentrated hydrochloric acid. To the hot solution 3 g. of powdered zinc was added with stirring and then 2 g. of powdered stannous chloride. The solution was allowed to boil for ten minutes and then cooled. Ammonium hydroxide was added to precipitate the zinc and tin salts and free amine. The solid was filtered and extracted with acetone, which dissolved the amine from the mixture. The amine was purified by crystallization from acetone–water mixture. It formed yellow crystals melting at 250–253°. The yield was 2 g. (74%).

Anal. Calcd. for $C_{16}H_{20}F_2N_4$: N, 18.30. Found: Kjeldahl N, 18.02.

Attempts to Prepare Suitable Salts of **3,5,3′,5′-Tetramethyl-2,2′-difluoro-4,6,4′,6′-tetraaminodiphenyl.**—Attempts were made to prepare salts of the tetraamine with *d*-camphorsulfonic acid, d-bromocamphorsulfonic acid and d-tartaric acid. The following solvents were tried: water, acetone, chloroform, petroleum ether, alcohol, ethyl acetate. pyridine and methyl alcohol. In no case did a crystalline salt result. The salts were either too soluble or, when thrown out of solution with some solvent, such as petroleum ether, came out as gummy precipitates. Both di- and tetra-salts were tried for the three acids.

Summary

1. The preparation of 3,5,3′,5′-tetramethyl-2,2′-difluoro-6,6′-diaminodiphenyl is described. The compound was resolved through the dicamphorsulfonate salt.

2. The active forms racemized readily by heating in a neutral solvent such as ethyl or methyl alcohol or more rapidly in glacial acetic acid.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE EFFECTS OF ACTIVATED AND NON-ACTIVATED MAGNESIUM-COPPER ALLOY ON THE YIELDS OF SOME ORGANOMAGNESIUM HALIDES

BY HENRY GILMAN AND E. A. ZOELLNER

RECEIVED FEBRUARY 2, 1931 PUBLISHED APRIL 6, 1931

Introduction

Activated magnesium-copper alloys containing 12.75[1] and 14.5%[2] of copper are apparently the best known catalysts for initiating reactions between RX compounds and magnesium in ether.[3] It has always been recommended that a small quantity of the catalyst be used to start the reaction, and that subsequently the reaction with the major part of the RX compound be carried out with ordinary magnesium. However, in studies on the preparation of the di-Grignard reagent from *p*-dibromobenzene,[4] it was observed that the highest yield of terephthalic acid (obtained subsequent to carbonation) resulted when a large excess of the activated alloy was used. This and the peculiar effects of the activated alloy and of varying quantities of iodine on the preparation and the yields of phenylmagnesium chloride[5] and other RMgX compounds was the basis for the statement: "Related unusual results with other RX compounds using varying quantities of iodine and alloy will be reported later."[5] We are now reporting some of these results from an as yet uncompleted study. The following paper on the capture of free radicals describes some additional experiments[6] concerned with the effects of an excess of iodine on the yields of some RMgX compounds.

The results here reported indicate that an equivalent of the alloy, either as such or after activation with iodine, decreases the yields of some typical Grignard reagents. The decrease is generally greater with the activated alloy. However, an excess of either the activated or non-activated alloy appears to increase the yield in some cases to those values obtainable when ordinary magnesium turnings or powder is used. For all practical purposes these variations in yield with the use of the alloy are without essential significance because only a very small quantity (usually 0.2 g.) of the activated alloy is used to initiate the reaction. This is established by experiments in which **0.19** to **0.51** g. of activated 12.75% alloy was used at first, the reaction with RX compound being

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[1] Gilman, Peterson and Schulze, *Rec. trav. chim.*, 47, 19 (1928).

[2] Gilman and Heck, *Bull. soc. chim.*, 45, 250 (1929).

[3] References to some of the applications by others of the activated alloy are: Hurd and Webb, THIS JOURNAL, 49, 546 (1927); Shepard, Winslow and Johnson, *ibid.*, 52, 2089 (1930).

[4] Gilman, Beaber and Jones, *Rec. trav. chim.*, 48, 597 (1929).

[5] Gilman and St. John, *ibid.*, 49, 717 (1930).

then completed with 1.1 atoms of ordinary magnesium turnings. With 0.19 g. of the activated alloy and n-butyl bromide the yield was 1–4% below normal, and the drop increased to 7% when 0.51 g. of activated alloy was used; with 0.25 g. of activated alloy and benzyl chloride, the yield was decreased 0–3%; and with 0.19 or 0.48 g. of activated alloy and bromobenzene the yield was unaffected.

The depression of the yield is probably not due to a reaction between the alloy and RMgX compound already formed, because in one experiment 1.5 g. of the 12.75% alloy when refluxed for ten minutes with preformed n-butylmagnesium bromide did not lower the yield within experimental error. The drop in yield when more than the recommended quantity of activated alloy is used may be due in part to the iodine or magnesium iodide contained therein, because the following paper shows that iodine or magnesium iodide when used in more than a very small amount or less than a full equivalent also lowers the yield of some Grignard reagents. It appears that a very small, and yet effective, quantity of either iodine or the activated alloy is without essential effect on the yield.

Experimental Part

The apparatus and general technique was that used in related studies.[6] The powdered alloy, as such or activated, was covered with 5 cc. of ether; then 20 drops of the pure RX compound and a crystal of iodine (always used with the non-activated alloy) was added. The mixture was heated for ten minutes by means of a water-bath at 45°. Then the remainder of the halide (a total of 0.05 mole) mixed with 25 cc. of ether, was added over a period of thirty minutes with stirring. After all of the halide had been added, the reaction mixture was stirred for an additional ten minutes.

TABLE I

YIELDS OF RMgX COMPOUNDS FROM UNACTIVATED AND ACTIVATED ALLOYS

Halide (0.5 mole)	Unactivated alloy G.[a]	Unactivated alloy % Yield, RMgX[b]	Activated alloy G.[c]	Activated alloy % Yield, RMgX[b]	Ordinary Mg turnings. % Yield RMgX[d]
n-C_4H_9Br	1.5	55.4,55.8(63.1)"	2	62.8	94
n-C_4H_9Br			3	67.9	
n-C_4H_9Br			5	80	
$C_6H_5CH_2Cl$	1.5	74.8 (83)[e]			93.1
$C_6H_5CH_2Cl$	2.0	89.5[f]	2	72.6	
C_6H_5Br	1.6	82.3, 83.9, 83.7 (88.8)[e]	2	79	94.7[d]
C_6H_5Br	2.0	94	3	97.8	
C_6H_5Br			5	98.7	
p-$CH_3C_6H_4Br$	1.5	87.8			86.9
p-$CH_3C_6H_4Br$	2.0	92	2	78.8	

[a] One equivalent or 0.05 mole of the alloy is 1.38 g.

[b] Each percentage yield listed is an average of at least two analyses made from one preparation.

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[6] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1676 (1929).

[c] The alloy used here was re-activated. In a few experiments carried out **with** activated alloy which was exposed to a somewhat humid atmosphere for twenty-five minutes after activation and then used directly without re-activation, the yields of *n*-butylmagnesium bromide from *2.0* g. of such alloy were **43.9** and 45%, and bromobenzene did not react. One equivalent of the activated alloy is *1.67* g.

[d] These percentages are taken from the studies described in Ref. 6, wherein ordinary magnesium *turnings* were used. They are, therefore, not comparable **with** the results obtained with the powdered alloy. This finds support in an experiment carried out during the present studies where the yield of phenylmagnesium bromide prepared from **1.33** g. of 100-mesh ordinary magnesium was 97.3%. See, also, Gilman and Fothergill, *Iowa State Coll. J. of Sci.*, *4*, *351* (1930), for the effect of an excess of fine magnesium on the yields of some Grignard reagents. The smaller drop in yield with an excess of the alloy may be due, in part, to the essential presence of an excess of fine magnesium.

[e] The percentages in parentheses are those obtained **with** the 12.75% copper-magnesium alloy of 30–80 mesh. In all other cases the alloy used contained 11.25% copper, and was of *60–200* mesh.

[f] With 6 g. of 12.75% copper–magnesium alloy of 30–80 mesh the yield of benzylmagnesium chloride was practically equal to that obtained with turnings of ordinary magnesium.

Summary

When equivalent quantities of copper–magnesium alloy are used alone, either in the activated or non-activated condition, the yields of some Grignard reagents are lowered. However, small, but effective, quantities of the activated alloy appear to have no significant effect on the yield. The other more commonly used catalyst, iodine, apparently has the same general effect as the alloy on the yields of some Grignard reagents (see following paper).

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF ORGANOMAGNESIUM HALIDES IN THE PRESENCE OF MAGNESIUM IODIDE. STUDIES ON THE CAPTURE OF FREE RADICALS

BY HENRY GILMAN AND E. A. ZOELLNER

RECEIVED FEBRUARY 2, 1931 PUBLISHED APRIL 6, 1931

Introduction

One of the current interpretations of the preparation of Grignard reagents involves the prior or intermediate formation of free radicals, after the following representation.

$$\mathrm{RX} + \mathrm{Mg} \longrightarrow \mathrm{R—} + \mathrm{—MgX} \tag{I}$$
$$\mathrm{R—} + \mathrm{—MgX} \longrightarrow \mathrm{RMgX} \tag{II}$$

There are several kinds of evidence for the intermediate formation of free radicals (R—) in accordance with Reaction I. The side reactions that invariably accompany the preparation of RMgX compounds, from RX compounds and magnesium, are best explained by the coupling, disproportionation and rearrangement reactions of the free radicals.[1] Furthermore, there is direct experimental evidence in support of Reaction II, inasmuch as it has been shown[2] that triarylmethyls, like $(C_6H_5)_3C—$, will combine with the hypothetical —MgX or its equivalent (the binary system, Mg + MgX_2, of Gomberg) to give triphenylmethylmagnesium halide, $(C_6H_5)_3CMgX$.

However, because triarylmethyls are, in a sense, a special class of free radicals, it was felt that a more complete case for Reaction II would be had if another type of free radical, as yet not isolated, were captured incidental to the formation of RMgX compounds. For this purpose, a study was first made of the reaction between *tert.*-butyl chloride and magnesium in either. Under ordinary conditions it is very difficult to get a satisfactory yield of *tert.*-butylmagnesium chloride[3] because of the marked tendency of the hypothetical intermediate *tert.*-butyl radicals to undergo coupling and, particularly, disproportionation to isobutane and isobutylene.

One way of capturing the *tert.*-butyl radicals is to have present, during the reaction between *tert.*-butyl chloride and magnesium, the —MgX (or the binary system, Mg + MgX_2). A procedure of this kind was successful in contributing to the improvement of the yield of triphenylmethylmagnesium chloride;[4] and, as already stated,[2] the independent systems, R— and —MgX, have been combined to give triphenylmethylmagnesium halides. When, however, this principle was employed in the preparation of *tert.*-butylmagnesium chloride we either did not capture the intermediate *tert.*-butyl radical, or having captured it we did not hold it for long because the yields of *tert.*-butylmagnesium chloride were, in general, actually reduced. In short, the binary system (Mg + MgI_2) did not make it possible to obtain a yield of *tert.*-butylmagnesium halide in excess of that obtained under optimal conditions when none of the binary system was purposefully added; but a trace of iodine (or of MgI_2 or (Mg + MgI_2)) or a full equivalent of the binary system did give a yield equal to that obtained when no magnesium iodide was added, and intermediate quantities depressed the yield—the greatest lowering being observed with about 0.25 equivalent of the binary system per equivalent of RX compound. This depression of yield very probably occurs in the early stages of the formation of the RMgX compound, inasmuch as magnesium or magnesium iodide or a combination of the two is without essential effect on the *tert.*-butylmagnesium chloride after it is once formed. Apparently the same sort of a depression, but to a less marked extent,

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[1] A recent study with leading literature references is Gilman and St. John, THIS JOURNAL. 52, 5017 (1930).

[2] Gilman and Fothergill, *ibid.*, 51, 3152 (1929); Gomberg and Bachmann, *ibid.*. 52, 2455 (1930); Bachmann, ibid., 52, 3287, 4412 (1930).

[3] Gilman and Zoellner, *ibid.*, 50, 425 (1928); *Rec. trav. chim.*, 47, 1058 (1928).

[4] Gilman and Zoellner, THIS JOURNAL, 51, 3493 (1929).

occurs with n-butylmagnesium bromide. It would be unwise to generalize from these two illustrations because of the frequently observed distinct differences between apparently related organomagnesium halides.

From the preliminary report now made, it follows that the generally used catalyst (iodine) has a deleterious effect on the yield unless used in very small quantities or in very large quantities. A like phenomenon is reported in the preceding paper,[5] when another more recent catalyst, the activated magnesium–copper alloys, is used. Fortunately, these effects are of no apparent serious moment from a practical viewpoint because the catalysts are almost always used in very small quantities merely to initiate reaction between a part of the RX compound and magnesium. In this connection it is interesting to recall that the time required to prepare phenylmagnesium chloride in ether solution decreases in a regular manner with the increase of iodine.[6]

Experimental Part

The apparatus and general technique was that used in related studies.' In the n-butylmagnesium bromide experiments the 30–80 mesh magnesium was first covered with 16 cc. of ether; then the selected quantity of iodine was added; when the iodine color disappeared, 20 drops of the n-butyl bromide was added directly without a solvent; the mixture was then refluxed for ten minutes; and, finally, the remainder of the halide (totaling 0.05 mole) in 21 cc. of ether was added with stirring at a uniform rate over one hour.

A variation of this procedure was used with the *tert.*-butylmagnesium chloride experiments. Because preliminary experiments showed that erratic results generally followed the addition of the chloride to the magnesium and magnesium iodide in ether, a part of the selected quantity of iodine was added subsequent to the formation of the major portion of magnesium iodide and subsequent to the addition of 20 drops of the chloride. In this manner the reaction between the *tert.*-butyl chloride and magnesium set in smoothly and there was no difficulty in getting concordant results. With each halide the quantity of fine magnesium used was one atom equivalent for each atom equivalent of iodine, in addition to one atom per mole of n-butyl bromide and three atoms per mole of *tert.*-butyl chloride.

The results of the experiments are contained in Table I. The average values are those of at least two preparations from each of which at least two aliquots were removed for titration, The agreements were of an uncommonly high order when one considers the great sensitivity of an RMgX compound like *tert.*-butylmagnesium chloride.

[5] Gilman and Zoellner, THIS JOURNAL, 53, 1581 (1931).

[6] Gilman and St. John, Rec. *trav. chim.*, 49, 717 (1930).

[7] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1576 (1929).

A like degree of duplicability of results with *tert.*-butylmagnesium iodide prepared in the presence of magnesium iodide was not observed in a few preliminary experiments. Here the yields of RMgI compound in two independent preparations using 0.08 g. or 0.0125 atom equivalent of iodine were 57.0 and 52.3%; and with 6.35 g. or 1.0 atom equivalent of iodine, the yields were 55.1 and 58.4%. These experiments with the iodide were carried out because of the possibility of magnesium iodide reacting with *tert.*-butyl chloride or *tert.*-butylmagnesium chloride to give *tert.*-butylmagnesium iodide.

TABLE I

EFFECT OF IODINE ON YIELD OF *n*-BUTYLMAGNESIUM BROMIDE AND *Tert.*-BUTYLMAGNESIUM CHLORIDE

Iodine			
G.	Atom equivalent	Av. % yield of n-C_4H_9MgBr	Av. % yield of $(CH_3)_3CMgCl$
None	None	**95.9"**	**83.3**
0.08	**0.0125**	**96.5"**	**83.6**
16	.025	..	**77.1**
.32	**.05**	**95.6**	**72.2**
.64	.1	**93.5**	**65.5'**
1 28	.2	**92.6**	**64.9**
1.90	.3[c]	**96.0**	**64.8**
2.54	.4	**94.9**	**71.8**
3.81	.6	**95.1**	**76.2**
6.35	1.0	**96.4**	**79.7**

[a] With **0.04** g. or **0.0063** equivalent of iodine the yield was **99%.** This unusually high value was checked. Further work is in progress on the effect of very small quantities of iodine on the yields of some other RMgX compounds.

[b] The low yield by titration was confirmed in a carbonation experiment with this relative quantity of iodine and with the **0.08** g. of iodine experiment which gave the 83.6% of Grignard reagent. It is interesting to note that this very high yield of RMgCl makes it possible to obtain trimethylacetic acid from it by carbonation in a **75%** yield.

[c] In the experiments using **0.3** or more atom equivalent of iodine, it was necessary to cover the magnesium with **35** cc. and not **16** cc. of ether. This, however, is without apparent effect on the relative yields because there was no change in yield when some of the preparations using less than **0.3** atom equivalent of iodine were carried out with 35 cc. instead of **16** cc. of ether.

Summary

In studies concerned with the capture of free radicals formed during the preparation of organomagnesium halides it has been shown that the quantity of iodine used to catalyze the formation of *tert.*-butylmagnesium chloride has a significant effect on the yield. There is no appreciable lowering of yield with a very small amount or a full atom equivalent of iodine. Another catalyst, the magnesium–copper alloy which is used with more refractory RX compounds, also appears to have a corresponding effect on the yields of other RMgX compounds.

AMES, IOWA

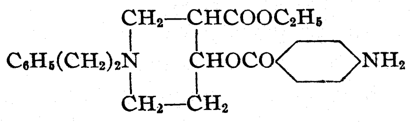
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

N-METHYL-N-PHENYLALKYL-AMINO-ALKYL BENZOATES AND PARA-AMINOBENZOATES

BY ARTHUR C. COPE AND S. M. MCELVAIN

RECEIVED FEBRUARY 2, 1931 PUBLISHED APRIL 6, 1931

All of the pharmacological data resulting from studies of the various types of local anesthetics which have been prepared in this Laboratory have shown very definitely that unusually powerful local anesthetic action is associated with those compounds containing a phenylalkyl group attached to the basic nitrogen atom. For example, 1-phenylethyl-3-carbethoxy-4-piperidyl *p*-aminobenzoate[1] (I) and 1-phenylethyl-4-piperidyl benzoate[2] (II) show, respectively, about two and seven times the power of cocaine for mucous membrane anesthesia.



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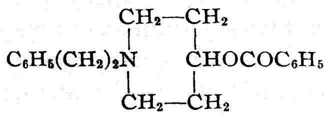

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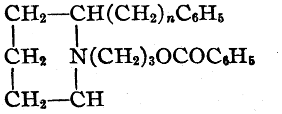
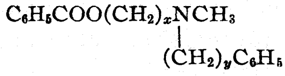


III



$C_6H_5COO(CH_2)_xNCH_3$ / $(CH_2)_yC_6H_5$

IV

Compounds of type III in which *n* is 1 or 2, were found[3] to be extraordinarily potent anesthetics, producing in 2% solution anesthesia of the rabbit's cornea that lasted from five to six days. When, however, the phenylalkyl substituent of the piperidine ring was shifted from the 2-position to the 4-position, there was a considerable diminution of the anesthetic action. This latter observation suggested that for maximum anesthetic effect the optimum number of carbon atoms in the chain between the phenyl group and the nitrogen atom would be less than five.

For this reason it seemed desirable to prepare and submit for pharmacological study a series of compounds of the procaine type in which various phenylalkyl groups would be attached to the nitrogen atom. This paper gives the preparation and a brief pharmacological report of a series of N-methyl-N-phenylalkyl-aminoalkyl benzoates (IV) in which x is 2 and 3 and y is varied from 1 to 4.

These compounds were prepared by condensing β-chloroethyl and γ-chloropropyl benzoates with the N-methylphenylalkylamines, which were

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[1] Thayer and McElvain, THIS JOURNAL, 49,2862 (1927).

[2] Bolyard and McElvain, *ibid.*, 51,922 (1929).

[3] Bailey and McElvain, *ibid.*, 52, 1633 (1930).

obtained from the hydrolysis of the N-methyl-N-phenylalkyl p-toluenesulfonamides. The benzoates were isolated as the hydrochlorides.

When an attempt was made to evaluate these benzoate hydrochlorides pharmacologically it was found that they produced an excessive amount of irritation in the rabbit's eye; consequently their anesthetic effect was so uncertain that any comparison on the basis of this property would have no particular meaning. For this reason the corresponding p-aminobenzoates were prepared in the hope that the increased basicity of the molecule would eliminate this undesirable property of the benzoates.[4] The *p*-aminobenzoates were obtained by the reduction of the corresponding *p*-nitrobenzoates. On account of the difficulties encountered in the purification of these *p*-aminobenzoates some were isolated as the monohydrochlorides and others as the dihydrochlorides.

Experimental Part

All boiling and melting points herein given are corrected.

Phenylalkylamines.—Benzylamine was prepared from benzyl chloride and hexamethylenetetramine according to the procedure of Delépine.[5] β-Phenylethylamine, γ-phenylpropylamine and δ-phenylbutylamine were prepared by the catalytic reduction of the corresponding cyanides by the method described by Carothers and Jones.[6]

N-Methylphenylalkylamines.—These amines were prepared from the phenylalkylamines by the method of Carothers, Bickford and Hurwitz.[7] This method involves the preparation of the N-phenylalkyl p-toluenesulfonamides, the methylation of these sulfonamides with methyl iodide to the N-methyl-N-phenylalkyl p-toluenesulfonamides and the hydrolysis of these latter compounds to the N-methylphenylalkylamines. The N-methylbenzylamine and N-methyl-β-phenylethylamine and the intermediate sulfonamides from which the amines were obtained have been described by these authors. The intermediate sulfonamides obtained in the preparation of N-methyl-γ-phenylpropylamine and N-methyl-δ-phenylbutylamine are new compounds and are summarized in Table I. There was one modification of the procedure necessary for the purification of the N-methyl-N-phenylalkyl p-toluenesulfonamides that should be noted. It was found that the N-methyl sulfonamides as obtained from the methylation reaction when the phenylalkyl group was phenylpropyl and phenylbutyl could not be caused to crystallize as they did when the phenylalkyl group was benzyl and phenylethyl. If, however, these oily sulfonamides were distilled under diminished pressure, the distillate solidified and could be recrystallized as easily as the lower homologs.

[4] *Cf.* McElvain, THIS JOURNAL, 48, 2239 (1926).

[5] Delépine, *Bull. soc. chim.*, [3] 17, 293 (1897).

[6] Carothers and Jones, THIS JOURNAL, 47, 3051 (1925).

[7] Carothers, Bickford and Hurwitz, *ibid.*, 49, 2908 (1927).

TABLE I

N-PHENYLALKYL *p*-TOLUENESULFONAMIDES AND N-METHYL N-PHENYLALKYL *p*-TOLUENESULFONAMIDES

N-substituents	Formula	M. p., °C.	B. p., °C.[a]	% S Calcd.	% S Found
γ-Phenylpropyl[b]	$C_{16}H_{19}O_2NS$	65.1–65.7		11.08	10.97
6-Phenylbutyl"	$C_{17}H_{21}O_2NS$	53.5–53.9	. . . .	10.57	10.47
Methyl and γ-phenylpropyl	$C_{17}H_{21}O_2NS$	41.8–42.4	234238 (3 mm.)	10.57	10.48
Methyl and 8-phenylbutyl	$C_{18}H_{23}O_2NS$	60.5–61.1	241–245 (2 mm.)	10.10	9.97

[a] These boiling points were uncorrected. [b] Along with this compound was obtained a small quantity of the N-phenylpropyl di-*p*-toluenesulfonamide, $C_{23}H_{25}O_4NS_2$, m. p. 113.3–113.7°, % S, calcd., 14.46; found, 14.51. [c] There was no appreciable quantity of the corresponding disulfonamide formed in this case.

The data for the N-methylphenylalkylamines and their hydrochlorides are shown in Table II. Since the hydrochloride of the N-methyl-β-phenylethylamine was found in this work to have a considerably higher melting point than that previously reported in the literature, it is included in Table II.

TABLE II

N-METHYLPHENYLALKYLAMINES AND THEIR HYDROCHLORIDES

No.	Phenylalkyl group	Formula	B. p., °C.	d_{25}^{25}	n_D^{25}
1	β-Phenylethyl	$C_9H_{13}N$	. . . .	. . . .	. . . .
2	γ-Phenylpropyl[b]	$C_{10}H_{15}N$	85.5–86.1 (5 mm.)	0.9205	1.50877
3	8-Phenylbutyl	$C_{11}H_{17}N$	95.0–95.4 (5 mm.)	0.9126	1.50350

No.	M_D Calcd.	M_D Found	% N Calcd.	% N Found	Hydrochloride, m. p., °C.	% Cl Calcd.	% Cl Found
1	. . .	. . .	. .	. .	164.1–164.9"	20.66	20.57
2	48.66	48.37	9.39	9.30	145.6–146.1	19.10	19.19
3	53.26	53.27	8.58	8.51	126.2–126.8	17.76	17.73

[a] The following melting points have been reported in the literature for this hydrochloride: 152–154" [Johnson and Guest, *Am. Chem. J.*, **42**, 340 (1909)]; 154–156" [Decker and Becker, *Ber.*, **45**, 2408 (1912)]; 156–157° [Decker and Becker, *Ann.*, **395**, 367 (1913)]; 155–157° [Hamilton and Robinson, *J. Chem. Soc.*, **109**, 1034 (1916)].

[b] This compound has been prepared [v. Braun, *Ber.*, **43**, 3216 (1910)] by the action of cyanogen bromide on N,N-dimethyl-γ-phenylpropylamine and was found to boil at 110° (17 mm.).

N-Methyl-N-phenylalkylaminoalkyl Benzoate Hydrochlorides.—Each of the secondary amines described in the preceding section was condensed with β-chloroethyl and γ-chloropropyl benzoates according to a method previously described.[8] The benzoates obtained were isolated as the hydrochlorides, which were formed by passing dry hydrogen chloride into an ether solution of the amino ester. These hydrochlorides were purified by recrystallization from the solvents indicated in Table III. The N-methyl-N-phenylalkyl-aminoethyl benzoates required additional purification by treatment with benzoyl chloride in the presence of sodium hydroxide in

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[8] McElvain, THIS JOURNAL, **49**, 2837 (1927).

order to remove unreacted secondary amine. The yields of pure hydrochlorides were 50–75% of the theoretical. The data for these compounds are summarized in Table III.

β-Chloroethyl and **γ-Chloropropyl *p*-Nitrobenzoates.**—These esters were prepared by heating ethylene chlorohydrin and trimethylene chlorohydrin with *p*-nitrobenzoyl chloride. The chloroethyl ester after purification melts at 55–56°.[9] The chloropropyl ester does not appear to have been described in the literature It boils at 168.5–169.5° (2 mm.), is a liquid at ordinary temperatures, d^{25}_{25} 1.3222, n^{25}_{D} 1.54736, M_D calcd., 57.91, found, 58.44. *Anal.* Calcd., Cl, 14.55. Found: Cl, 14.74

N-Methyl-N-phenylalkyl-aminoalkyl *p*-Nitrobenzoate Hydrochlorides.—While good yields of these hydrochlorides were obtained from the condensation of the chloro esters with N-methylbenzyl, β-phenylethyl, and δ-phenylbutylamines, the products of similar condensations with N-methyl-γ-phenylpropylamine could not be purified. Consequently the N-methyl-y-phenylpropylamine was condensed with ethylene and trimethylene chlorohydrins, and the tertiary amino alcohols thus produced were esterified with p-nitrobenzoyl chloride. This procedure gave the hydrochlorides of the *p*-nitrobenzoates of these amino alcohols in about 90% yields. The amino alcohols are described below.

TABLE III

N-METHYL-N-PHENYLALKYLAMINO-ALKYL BENZOATE HYDROCHLORIDES

$C_6H_5COO(CH_2)_xNCH_3$ / $C_6H_5(CH_2)_y$

x	y	Formula	M. p., °C.	Recryst. solvent	% Cl Calcd.	% Cl Found
2	1	$C_{17}H_{20}O_2NCl$	145.6–146.4	Ether + EtOH	11.60	11.72
2	2	$C_{18}H_{22}O_2NCl$	134.2–134.8 (Softens at 114)	EtOH	11.09	11.14
2	3	$C_{19}H_{24}O_2NCl$	106.3–107.1	*n*-BuOH	10.62	10.68
2	4	$C_{20}H_{26}O_2NCl$	106.9–107.5	*n*-BuOH	10.20	10.29
3	1	$C_{18}H_{22}O_2NCl$	145.4–146.3	EtOH	11.09	11.06
3	2	$C_{19}H_{24}O_2NCl$	128.8–129.4	EtOH	10.62	10.64
3	3	$C_{20}H_{26}O_2NCl$	117.5–118.3	*n*-BuOH	10.20	10.27
3	4	$C_{21}H_{28}O_2NCl$	124.7–125.7	*n*-BuOH	9.80	9.85

As in the case of the benzoates the condensation was more complete with y-chloropropyl p-nitrobenzoate than with β-chloroethyl *p*-nitrobenzoate, making purification of the product by treatment with benzoyl chloride as well as by recrystallization necessary in the latter case. The yields of purified products were 45–70% of the theoretical.

N-Methyl-N-y-phenylpropylaminoethanol.—Fen *g.* (0.1 mole) of N-methyl-γ-phenylpropylamine and 4.05 g. (0.05 mole) of ethylene chlorohydrin were condensed by heating for four hours at 100–120°. On diluting the reaction mixture with ether a yield of 9.35 g of **N-methyl-y-phenylpropylamine** hydrochloride was obtained after filtering and drying. The ether solution of the tertiary amino alcohol was dried over

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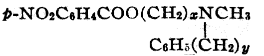
[9] Cf. *Friedländer*, 8,993 (1906).

TABLE IV

N-METHYL-N-PHENYLALKYLAMINOALKYL *p*-NITROBENZOATE HYDROCHLORIDES



$p\text{-}NO_2C_6H_4COO(CH_2)_xN(CH_3)(CH_2)_yC_6H_5$

x	*y*	Formula	M. p., °C.	Recryst. solvent	% Cl Calcd	% Cl Found
2	1	$C_{17}H_{19}O_4N_2Cl$	216.6–217.6	EtOH	10.11	10.12
2	2	$C_{18}H_{21}O_4N_2Cl$	170.9–171.9	EtOH + ether	9.72	9.70
2	3	$C_{19}H_{23}O_4N_2Cl$	122.6–123.6	*n*-BuOH + ether	9.36	9.38
2	4	$C_{20}H_{25}O_4N_2Cl$	120.6–121.6	*n*-BuOH + ether	9.03	9.08
3	1	$C_{18}H_{21}O_4N_2Cl$	206.6–207.4	EtOH	9.72	9.73
3	2	$C_{19}H_{23}O_4N_2Cl$	147.2–148.2	EtOH + ether	9.36	9.48
3	3	$C_{20}H_{25}O_4N_2Cl$	99.5–100.3	Acetone	9.03	8.98
3	4	$C_{21}H_{27}O_4N_2Cl$	159.3–160.3	*n*-BuOH + ether	8.71	8.76

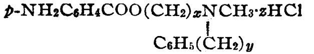
sodium sulfate and distilled under diminished pressure; yield, 7.30 g. (75.3%); b p 132.6–133.0° (5 mm.); d_{25}^{25} 0.9883; n_D^{25} 1.51723; M_D calcd. 59.38, found 59.15; calcd. for $C_{12}H_{19}ON$: N, 7.24; found: N, 7.10.

N-Methyl-N-γ-phenylpropylaminopropanol.—From 15 g. (0.10 mole) of N-methyl-y-phenylpropylamine and 4.75 g. (0.05 mole) of trimethylene chlorohydrin, 8.56 g. (82.973 of N-methyl-N-y-phenylpropylaminopropanol was obtained by the procedure described above: b. p. 147.3–147.9' (5 mm.); d_{25}^{25} 0.9785; n_D^{25} 1.51335; M_D calcd. 63.99, found 63.98. Calcd. for $C_{13}H_{21}ON$: N, 6.75; found: N, 6.57.

N-Methyl-N-phenylalkylaminoalkyl *p*-Aminobenzoate Hydrochlorides.—Those paminobenzoates which are tabulated in Table V as the monohydrochlorides were prepared by the catalytic reduction of the corresponding *p*-nitrobenzoates by a procedure previously described.[4] The other p-aminobenzoates shown in Table V could not be obtained crystalline from the catalytic reduction either as the monohydrochlorides or as the dihydrochlorides. It was possible, however, to obtain these aminobenzoates as crystalline dihydrochlorides from the reduction of the nitrobenzoates with iron. The procedure consisted simply of stirring the hydrochloride of the *p*-nitrobenzoate into a paste made from ten times its weight of iron powder, water, and a small amount of dilute hydrochloric acid until the heat of reaction subsided, extracting the free base with benzene, and precipitating the dihydrochloride from this benzene solution with dry hydrogen chloride. It was not possible to obtain an analytically pure

TABLE V

N-METHYL-N-PHENYLALKYL-AMINOALKYL *p*-AMINOBENZOATE HYDROCHLORIDES



$p\text{-}NH_2C_6H_4COO(CH_2)_xN(CH_3)(CH_2)_yC_6H_5\cdot zHCl$

x	*y*	*z*	Formula	M. p., °C.	Recryst. solvent	% Cl Calcd.	% Cl Found
2	1	2	$C_{17}H_{22}O_2N_2Cl_2$	209.6–210.6	EtOH	19.85	19.79
2	2	2	$C_{18}H_{24}O_2N_2Cl_2$	245.2–247.4	EtOH	19.10	18.99
2	3	2	$C_{19}H_{26}O_2N_2Cl_2$	182.3–184.3	EtOH + ether	18.41	18.26
3	1	2	$C_{18}H_{24}O_2N_2Cl_2$	219.1–220.1	EtOH	19.10	18.91
3	2	1	$C_{19}H_{25}O_2N_2Cl$	190.7–192.2	EtOH + ether	10.16	10.14
3	3	1	$C_{20}H_{27}O_2N_2Cl$	178.8–179.8	EtOH	9.77	9.76
3	4	1	$C_{21}H_{29}O_2N_2Cl$	156.0–158.0	Acetone	9.41	9.39

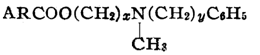
hydrochloride of N-methyl-N-6-phenylbutylaminoethyl *p*-aminobenzoate from either of the reduction procedures. The yields of the monohydrochlorides after purification from the catalytic reduction were 60–70% and of the dihydrochlorides from the iron reduction 50–95% of those theoretically possible. The hydrochlorides of the p-aminobenzoates are summarized in Table V.

Pharmacological Report

The N-methyl-N-phenylalkylamino-alkyl benzoates and *p*-aminobenzoates are being studied pharmacologically by Mr. Charles L. Rose of The Lilly Research Laboratories, Indianapolis, Indiana. The preliminary pharmacological observations are summarized in Table VI. The corneal anesthesia values were determined by application of a solution of the anesthetic to the rabbit's cornea and noting the duration of anesthesia. In this determination a 2% solution of the benzoate hydrochlorides was used in each case, but with the p-aminobenzoates a 1% solution of the monohydrochloride was used on account of the low solubility of certain members of this series. The monohydrochlorides of those p-aminobenzoates which are listed in Table V as the dihydrochlorides were obtained by dissolving the latter salt in water and titrating off one of the

TABLE VI

PHARMACOLOGICAL DATA: N-METHYL-N-PHENYLALKYLAMINOALKYL BENZOATES AND *p*-AMINOBENZOATES

 $\mathrm{ARCOO(CH_2)_xN(CH_3)(CH_2)_yC_6H_5}$ AR	x	y	Av. duration of anesthesia Corneal, minutes	 Infiltration, minutes	Subcutaneous toxicity to white mice (mg./kg.) M. L. D.	Intravenous toxicity to white rats (mg./kg.) M. L. D.
Phenyl	2	1	7[a]	20[b]	3500	45
Phenyl	2	2	7	15	2500	50
Phenyl	2	3	10	12	3000	50
Phenyl	2	4	3	29	3000	50
Phenyl	3	1	9	17	2500	45
Phenyl	3	2	13	21	1800	35
Phenyl	3	3	15	34	1500	60
Phenyl	3	4	16	18	2000	50
p-Amino phenyl	2	1	16		400	50
p-Amino phenyl	2	2	60		300	30
p-Amino phenyl	2	3	27		200	22.5
p-Amino phenyl	3	1	21		150	30
p-Amino phenyl	3	2	33		150	14
p-Amino phenyl	3	3	32		200	24
p-Amino phenyl	3	4	114		200	22
Cocaine			29		150	17.5
Procaine			0	..	1000	40

[a] For those compounds in which AR is phenyl a 2% solution was used and for those in which AR is p-aminophenyl a 1% solution was used. [b] The doses producing the values in this column were 0.1 cc. of a 1% solution.

halogen acid molecules with standard alkali. On account of the uncertain corneal anesthesia values obtained with the benzoate hydrochlorides, the infiltration anesthesia values for these compounds as determined from intracutaneous injection into the guinea pig are included in Table VI. The toxicities as determined by subcutaneous injection into white mice and by intravenous injection into white rats are reported as minimum lethal doses in milligrams per kilogram body weight. The anesthetic and toxicity values for cocaine and procaine are included in the table for comparison.

Discussion of the Pharmacological Data.—As pointed out above, the excessive amount of irritation which was caused in the case of each of the benzoate hydrochlorides when applied to the rabbit's cornea does not allow for very much, if any, significance to be attached to these values in the above table. This undesirable property which was so pronounced in the benzoate series is entirely absent in the p-aminobenzoate series.

There is some indication from the data in Table VI that maximum anesthetic effect is associated with certain intermediate sizes of the phenylalkyl groups in some of the more closely related groups of compounds. For example, with the aminopropyl benzoates (AR is phenyl and x is 3) the maximum infiltration anesthetic effect is shown by the phenylpropyl group (where y is 3), and in the p-aminobenzoate group where x is 2 the maximum corneal anesthesia value is found where the nitrogen substituent is a phenylethyl group. Unfortunately for any generalization a similar relationship does not exist in the infiltration anesthesia values for the aminoethyl benzoates (AR is phenyl, x is 2) or in the corneal anesthesia values for the aminopropyl p-arninobenzoates (AR is p-aminophenyl, x is 3).

The extremely low toxicities of the N-methyl-N-phenyl-alkyl benzoates are worthy of note. As a group they are much less toxic than procaine both subcutaneously and intravenously. The corresponding p-aminobenzoates show a decidedly different and most unusual toxic effect. Their intravenous toxicities are rather low as a group, certain ones approaching the toxicity of procaine. The subcutaneous toxicities, however, are considerably' higher than would be expected from the intravenous values. An outstanding case is the N-methyl-N-benzylaminoethyl *p*-aminobenzoate. This compound is about 80% as toxic as procaine intravenously but is over twice as toxic subcutaneously. It is quite probable that this unusual behavior is due to the very rapid absorption of the p-aminobenzoates when they are injected subcutaneously.

Summary

A series of local anesthetics of the formula, $ARCOO(CH_2)_xN(CH_3)(CH_2)_yC_6H_5$, in which AR is phenyl and p-aminophenyl, x is 2 and 3, and y is varied from 1 to 4 has been prepared and described.

A brief report of the preliminary pharmacological study of these compounds together with a discussion of some relationships between their structure and pharmacological action is given.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY OF AMHERST COLLEGE]

PREPARATION OF DICHLOROACETIC ACID

BY HOWARD WATERS DOUGHTY AND GERHARD JULIUS DERGE[1]

RECEIVED FEBRUARY 3, 1931 PUBLISHED APRIL 6, 1931

In **1925** Doughty and Black[e] described the preparation of dichloroacetic acid by the reaction of copper powder with trichloroacetic acid or aniline trichloroacetate, in benzene. They obtained yields of aniline dichloroacetate, from which they prepared dichloroacetic acid, up to 75% of the theoretical. Other experimenters have used this method with varying success, and the irregularity of yield, as reported privately to the senior author, has led to a reëxamination of the procedure by the present authors. We first repeated the procedure of Doughty and Black and found that when insufficient hydrogen chloride is used for complete saturation in precipitating the copper chlorides and aniline hydrochloride, a complex substance containing copper and aniline is formed, which is unsatisfactory to work with. We did, however, obtain yields from 50 to **70%** of the theoretical, without making especial effort for maximum yield.

The reaction of trichloroacetic acid in aqueous solution on various metals has been studied to some extent in this Laboratory, and in **1929** Doughty and Lacoss[3] showed that the reaction between trichloroacetic acid and zinc in water proceeds quantitatively according to the equation

$$2CCl_3COOH + 2Zn = (CCl_2HCOO)_2Zn + ZnCl_2$$

and it has also been found* that cadmium, iron and copper act similarly with trichloroacetic acid in aqueous solution, while with magnesium and aluminum considerable quantities of hydrogen are formed and the reaction is evidently more complicated. In view of the difficulties which have been reported in obtaining consistent yields by the method of Doughty and Black, we decided to investigate the reaction in aqueous solution and, if practicable, develop a procedure for the preparation of dichloroacetic acid, though earlier attempts in this direction have given low yields. It seemed possible that the hydrolysis of trichloroacetic acid to chloroform and

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[1] The work here reported is in partial fulfilment of the requirement for "Honors in Chemistry" by Gerhard J. Derge. The work has been checked by Howard W. Jones, to whom we wish to express our thanks.

[2] Doughty and Black, THIS JOURNAL, 47,1091 (1925).

[3] Doughty and Lacoss, *ibid.*, 51,852 (1929).

[4] Unpublished work by H. W. Doughty.

carbon dioxide might be the cause of the low yield, and that proper control of temperature might give better results. We therefore made a preliminary study of the hydrolysis of trichloroacetic acid as affected by temperature.

Hydrolysis of Trichloroacetic Acid.—At room temperature hydrolysis is very slow. A 1.007 molar solution of trichloroacetic acid in water was prepared on February 13. On May 10 it was found to be 0.9856 molar. Other determinations were made at approximately 60 and at 100°. The temperature control at 60° was within two or three degrees, and at the higher temperature the solution was simply boiled with return condenser, portions being removed from time to time for analysis. The velocity constants were calculated as for a first order reaction, as the water concentration remains constant, using the equation $k = (1/t) \log [a/(a-x)]$, where t is elapsed time in minutes, a is the original concentration of trichloroacetic acid, x is the moles of chloroform per liter produced, and therefore $a - x$ is the concentration of trichloroacetic acid at time t.

TABLE I

HYDROLYSIS OF TRICHLOROACETIC ACID AT 100°

t	Concentration of CCLCOOEI + HCI	Concentration of HCl	$(a - x) =$ Concentration of CCl_3COOH	k
0	0.9656 = a	0.0000	0.9656	
30	.7490	.0105	.7385	0.0039
90	.4669	.0190	.4479	.0037
330	.0774	.0341	.0433	.0040

Apparently there was some hydrolysis of the trichloromethyl group, either of the trichloroacetic acid or the resultant chloroform, as indicated by the hydrochloric acid found. Correction was made for this by subtracting the concentration of hydrochloric acid from the total acid found.

TABLE II

HYDROLYSIS OF TRICHLOROACETIC ACID AT 60°

t	Concentration of $CCl_3COOH + HCl$	Concentration of HCl	$(a - x) =$ Concentration of CCl_3COOH	k
0	0.9469	0.000	0.9469	
90	.9332	.0040	.9292	0.000091
240	.9101	.0087	.9014	.000088

From these results the temperature coefficient of the hydrolysis is found to be $k_{(t+10)}/k_t = 2.576$. Evidently the loss by hydrolysis would be relatively small if the temperature is kept at about 60° during the reaction of trichloroacetic acid with copper. The following procedure was accordingly adopted.

Preparation of Dichloroacetic Acid.—A solution of 55 g. (one-third mole) of trichloroacetic acid in 450 cc. of water is placed in a one-liter flask, which is provided with a mechanical stirrer and thermometer. The stirring is started at once, 35 g. of copper powder (approximately 0.5 gram atomic weight) is added, and the temperature raised to 60°. (As stated in previous communications, we have found the so-called "dark copper bronze" powder used by decorators to be very satisfactory for use in this connection.) The reaction is quite strongly exothermic, and the heating may be discontinued after the desired temperature, 60°, is reached. After stirring for about one hour and a half, the solution is heated to boiling for about one hour, during which the solid portion of the mixture changes in color from a dirty green to white, due to the action of the excess of copper on the cupric chloride, precipitating cuprous chloride. This reaction always occurs to some extent, and unless an excess of copper is used over the amount calculated in terms of the corresponding reaction with zinc, trichloroacetic acid is found in the product. After the precipitate has become white and shows no excess copper, the mixture is cooled to allow maximum separation of cuprous chloride. It is then filtered and washed with small amounts of cold water. The filtrate is now saturated with hydrogen sulfide until the precipitation of copper sulfides is complete. The precipitate is removed by filtering with suction, washed, and the filtrate, which should be colorless or slightly yellow, is distilled under diminished pressure. The portion which boils above 50° at 20 mm. is fractionated at 20 mm. Dichloroacetic acid boils at 102° (20 mm.). The whole dilute solution of dichloroacetic acid is distilled under diminished pressure, as otherwise the yield is not satisfactory. This appears to be due to the presence of the hydrochloric acid formed during the precipitation of the copper sulfides, as experiment has shown that at 100° the hydrolysis of dichloroacetic acid is not more than 10% in twenty-four hours. The yield by this procedure is about 80%.

To check the purity of the product, the acid thus prepared was analyzed by titration with sodium hydroxide, and 2.1006 mg. moles of dichloracetic acid required 2.0848 mg. moles of sodium hydroxide, indicating 99.25% purity. The density of the acid was found, by pycnometer, to be d_{22}^{22} 1.5594. Perkin[5] gives d_4^4 1.5843 and d_{25}^{25} 1.5604, and Doughty and Black[2] found d_{20}^{20} 1.5666 and d_4^{20} 1.5634.

The melting point of our acid was between 5 and 6°. The melting point of dichloroacetic acid as given in successive issues of Beilstein is variously recorded as −4, −10.8, +10.8° and finally as reported by Kendall,[6] −4.1° and +9.7° according to the rate of cooling and the degree of undercooling. Under ordinary conditions, therefore, the melting point of this acid cannot be regarded as a criterion of purity.

Summary

A simple and convenient method is described for the preparation of dichloroacetic acid by the reaction of copper with trichloroacetic acid in aqueous solution.

The hydrolysis of trichloroacetic acid has been studied at 60° and at 100° and the temperature coefficient found to be *2.576.*

AMHERST, MASSACHUSETTS

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[5] Perkin, J. *Chem. Soc.*, 65,422 (1894).

[6] Kendall, THIS JOURNAL, 36,1230 (1914).

[CONTRIBUTION NO. 107 FROM CARBOHYDRATE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

NEW SOURCES OF INULIN[1]

BY E. YANOVSKY AND R. M. KINGSBURY

RECEIVED FEBRUARY 3, 1931 PUBLISHED APRIL 6, 1931

In spite of the fact that inulin was discovered 125 years ago[2] and that voluminous literature has appeared since that time,[3] both the chemical nature of inulin and its physiological significance are but little understood.

Inulin, prepared originally from elecampane (*Inula helenium*), has been since detected in a great many plants, mostly of the family *Compositae*. For actual preparation of quantities of inulin, only a few plants have been used, among which dahlia (Dahlia *variabilis*), Jerusalem artichoke (*Helianthus tuberosus*), chicory (*Cichorium intybus*) and dandelion (*Taraxacum officinale*) are by far the most important. Dean[4] prepared inulin from burdock roots (*Lappa minor*) and the roots of goldenrod (*Solidago*).

Although the similarity of inulin prepared from different sources was evident, the identity of products of different origin was averred by some investigators and denied by others. The question was finally settled by Tanret,[5] who fractionated the inulin from the Jerusalem artichoke into five—as he believed—distinct compounds, varying in their molecular complexity, specific rotation (−17 to −39°), and the degree of solubility in water and dilute alcohol. Some doubt may be felt as to the existence of Tanret's compounds as definite chemical individuals; the existence, however, of a series of complex anhydrides of levulose—by whatever name we may call them—was established beyond doubt. Dean[4] suggested that the name inulin be limited to the fraction of specific rotation between −33 and −40°, and that the compounds of lower levorotatory power and higher solubility be called levulins. This suggestion, however, does not seem to constitute an improvement over Tanret's classification, since it is apparent that a compound whose specific rotation varies 7° cannot be called a chemical individual. For the time being, until the chemistry of the group

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[1] Read at the meeting of the American Association for the Advancement of Science, December 30, 1930, Cleveland, Ohio.

[2] V. Rose-Gehlen's "*Neues Allgem.* J. *Chem.*," 3, 217 (1804); also Nicholson's "*J. Nat. Phil. Chem.*," 12, 97 (1805).

[3] No attempt will be made in this article to review the literature on the subject. The reader is referred to Dragendorff's "Materialien zu einer Monographie des Inulins," 1870; and articles by Kiliani, *Ann.*, 205, 145 (1880); Willaman, *J. Biol. Chem.*, 51, 275 (1922); Harding, Sugar. 636 1923; and others, who quote extensively the literature on the subject.

[4] Dean, *Am. Chem.* J., 32, 69 (1904).

[5] Tanret, *Bull. soc. chim.*, 9, 200, 227, 622 (1893); also Colin, *Rev. Gen. Bot.*, 31, 75, 179, 229, 277 (1919).

is better known, we may speak of the inulin group or inulin compounds as comprising all complex anhydrides of levulose.

In view of the fact that the practical sources of inulin are limited in number, we thought it would be advisable to call the attention of investigators in this line to some new sources of inulin, found in the course of systematic investigation of carbohydrates of uncultivated plants indigenous to the United States.

Inulin from Camas Roots.—Camas roots—*Quamasia quamash* (Pursh) Coville (*Camassia esculenta* Lindl.)[6]—were extensively and to a certain extent still are used for food by the North American Indians. The roots were cooked in stone-lined pits in the ground to a sweet, molasses-like sirup, or were roasted and ground into flour. Camas can be found in large quantities in Colorado, Utah, Idaho, Montana, Washington, Oregon and California. It is used as an ornamental plant in France.[7]

Results of analyses of camas roots received from different parts of the country are given in Table I.[8]

TABLE I

ANALYSES OF CAMAS ROOTS

Source and date recd.	Moisture, %	Reducing sugar (calcd. as dextrose)		Non-reducing sugar (calcd. as sucrose)	
			On dry basis		On dry basis
Utah, August, 1929	50.5	2.8	5.7	22.0	44.4
California, January, 1930	64.3	1.3	3.6	18.7	52.4
Idaho, May, 1930	58.2	2.8	6.7	15.2	36.6
Oregon, May, 1930	66.0	3.0	8.8	11.6	34.1
Washington, June, 1930	68.0	2.2	6.9	13.3	41 6
Idaho, June, 1930	68.3	2.7	8.5	14.2	44.8
Montana, July, 1930	66.9	1.5	4.5	15.0	45.3
Oregon, July, 1930	67.3	3 8	11.6	16.9	51.7

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[6] Lewis and Clark Expedition, by E. Coues, 1893, pp. 952, 999; Pursh, "Flora Americae Septentrionalis," 1814, Vol. I, pp. 226–227; Brown, *Trans. Bot. Soc. Edinburgh*, 9, 378 (1868); Rep. Commiss. Agr. for 1870, p. 404; Palmer, *Am. J. Pharm.*, 50, 539 (1878); Newberry, *Pop. Sci. Monthly*, 32, 31 (1887); Havard, *Bull. Torrey Bot. Club*, 22, 98 (1895); Coville, *Contrib. U. S. Nat. Herbarium*, Vol. 5, No. 2 (1897); Blankinship, *Mont. Agr. Coll. Exp. Sta. Bull.*, *56* (1905); Spinden, *Mem. Am. Anthrop. Assn.*, Vol. II, pt. 3,200 (1908); Chamberlin, *Proc. Acad. Nat. Sci. Phila.*, **63**, 24 (1911), also *Mem. Am. Anthrop. Assn.*, Vol. II, pt. 5 (1911); Stout, *J. N. Y. Bot. Gard.*, 15, *50* (1914); Wilson, *Ottawa Naturalist*, 30, 17 (1916); McClintock, "Old Indian Trails," 1923, appendix; Anderson, "Trees and Shrubs of Brit. Col.," 1925.

[7] Bois, "Les plantes alimentaires chez tous les peuples," Paris, 1927.

[8] We wish to acknowledge our indebtedness for furnishing us with roots to Professor H. St. John, at the time with State College of Washington, Pullman, Wash., and to the following members of the U. S. Forest Service: R. H. Rutledge, Regional Forester, Ogden, Utah; S. W. Stoddard, Supervisor, Targhee National Forest, St. Anthony, Idaho; E. N. Kavanagh, Asst. Regional Forester, Portland, Ore.; G. D. Brown, Supervisor, Fremont National Forest, Lakeview, Ore.; Evan W. Kelley, Regional Forester, Missoula, Mont.; and K. D. Flock, Chief of Party, G-Surveys, Monarch, Mont.

An extract of camas root prepared for sugar analysis showed a rotation of –2.75′ V. in a 2-dm. tube. After hydrolysis, the rotation was –6.7°. The rotation of other solutions taken from different samples of roots was as follows

Before hydrolysis........ ...	–2.0°	–2.6"	–2.4°	–2.4°
After hydrolysis...... . .	–5.6°	–6.1°	–6.5°	–6.5"

When it is taken into consideration that the specific rotation of inulin is about –35° and the specific rotation of levulose is –92°, the figures given above indicate that most (if not all) of the "non-reducing sugar" in camas roots is present in the form of inulin. Both the root and its extract give a positive Seliwanoff's reaction.

Owing to the presence of pectin-like gum in camas roots, the usual extraction of inulin with water is inconvenient, and the following method was used.

Two hundred grams of bulbs, put through a meat chopper, was extracted by heating with 1 liter of 50% alcohol and a little calcium carbonate. It was then made up to 2 liters with 95% alcohol and filtered. Eighteen hundred cubic centimeters of the filtrate was evaporated to about 400 cc. The solution was treated with neutral lead acetate and, after filtering, deleaded either with hydrogen sulfide or sodium carbonate. It was then evaporated to a thin sirup, and several volumes of 95% alcohol was added. After a few hours the alcohol was poured off the precipitated gummy material and some absolute alcohol added. After the gum had hardened it was dried in vacuo at about 70°. The spongy material obtained was easily ground to a white powder. The yield was 30–31 g. Various preparations of the material thus obtained had a specific rotation of –23.0 to –29.0°; 80 to 90% of it was non-reducing sugar (inulin); 2 to 3% reducing sugar was present, and the rest was mostly moisture and ash. On dissolving the inulin in a very small amount of water and reprecipitating it with a large volume of alcohol, a product of specific rotation of –33.0′ was obtained. It had no trace of reducing sugar. The inulin thus obtained was *soluble* in *cold water and 60% alcohol.* The latter dissolves about 5% inulin at room temperature. It resembled somewhat the inulin from asphodel, described by Colin and Neyron de Méons,[9] although the asphodel inulin had a considerably lower specific rotation.

Inulin from Allium nuttallii S. Wats.—This variety of wild onion was used for food by various Indian tribes. The Cheyennes boiled it with meat.[10] A sample received from Nebraska (April, 1930) showed the following content of reducing and non-reducing sugars.

[9] Colin and Neyron de Méons, *Compt.* rend., 185, 1604 (1927).

[10] Grinnell, "The Cheyenne Indians." 1923, Vol. II, p. 171.

	%	On dry basis. %
Moisture	69.8	..
Reducing sugar	1.7	5.6
Non-reducing sugar	18.1	59.9

A solution of sugars prepared from the bulbs had a rotation of —5.5' V. in a 2-dm. tube. On hydrolysis the rotation changed to —12.5'. Seliwanoff's reaction was positive.

Two hundred grams of bulbs, put through a meat chopper, was extracted with about 2 liters of cold water. After filtering and washing the pulp, the solution was treated with neutral lead acetate. The excess of lead was removed with hydrogen sulfide. Excess hydrogen sulfide was removed by a stream of air. The solution was filtered with decolorizing carbon and evaporated in vacuo to a thin, colorless sirup. Several volumes of 95% alcohol was added. The amorphous precipitate was dried in vacuo. The yield was 25 g. of white powder. Without further purification the specific rotation was $[\alpha]^{20}_{\mathrm{D}}$ —31'. The inulin thus obtained was soluble in cold water and 70% alcohol (5% solution).

Both camas roots and wild onions belong to the family of *Liliaceae,* which has been little investigated for its inulin contents.[11]

The third source of inulin we came across—*Balsamorrhiza sagittata* (Pursh) Nutt—belongs to the family *Compositae,* known to contain many inulin-bearing plants. Although, at certain stages of growth, balsam root apparently contains a great deal of inulin,[12] it cannot be considered a very good practical source of inulin on account of the heavy bark and the woody structure of the root itself. The root, however, has been used for food and medicinal purposes by the Indians.[13]

The decorticated root had the following content of reducing and non-reducing sugars

Source and date recd.	Moisture, %	Reducing sugar (calcd. as dextrose)		Non-reducing sugar (calcd. as sucrose)	
			On dry basis		On dry basis
Utah, July, 1929	7.0	10 6	11.4	9.3	10.1
Wyoming, August, 1929	9.0	12.4	13.6	9.0	9.9
Utah, May, 1930	8.8	2.1	2.3	6.2	6.8

A solution of sugars prepared from the root had the optical rotation —1.2' V. in a 2-dm. tube. After hydrolysis the rotation was —3.3'.

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[11] Chevastelon [Dissertation, Paris, 1894, quoted through four-page abstract, J. *Pharm. Chim.*, 2, 83 (1895)] prepared from garlic inulin of sp. rot. −39°, very soluble in cold water and 70% alcohol. Similar preparations were made from hyacinth and other representatives of the Lily family.

[12] Inulin crystals were found by V. A. Pease, Associate Microscopist, Bureau of Chemistry and Soils, and George L. Keenan, Microanalyst, Food and Drug Administration, U. S. Department of Agriculture, in the course of histological and microchemical study of this plant (unpublished records).

[13] Yanovsky, THIS JOURNAL, 52, 3446 (1930).

Seliwanoff's reaction was positive. One hundred grams of powdered root was treated in the way described for *Allium nuttallii.* The inulin obtained was redissolved in water and reprecipitated with alcohol. The yield was 3.2 g. The specific rotation was –27.7°. The product was soluble in water, but less soluble in dilute alcohol than the inulin from camas or wild onions; 40% alcohol dissolved 5% of inulin.

Summary

1. Three new sources of inulin are described, two plants of the family of *Liliaceae* and one of the *Compositae.*
2. The specific rotation of inulin from these sources ranged from –28 to –33°. All products were soluble in water and dilute alcohol.
3. In the light of this work and that of Chevastelon, it appears that there is no correlation between the specific rotation and the solubility of inulin.
4. No claim is made that any of the products described was a definite chemical individual.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

IDENTIFICATION OF ALCOHOLS. PARA-NITROPHENYL URETHANS

BY R. L. SHRINER AND RICHARD F. B. COX

RECEIVED FEBRUARY 7, 1931 PUBLISHED APRIL 6, 1931

The common reagents used for the preparation of solid derivatives of the alcohols are 3,5-dinitrobenzoyl chloride, phenyl isocyanate and α-naphthyl isocyanate. Since the melting points of many of these derivatives of the common aliphatic alcohols are rather low, which makes them difficult to purify, and since the differences in the melting points of certain pairs of compounds are rather small, it was thought that a series of higher-melting derivatives would be of value. The present communication presents the data obtained on p-nitrophenyl urethans of the common aliphatic alcohols. Table I summarizes the properties of the new derivatives and also lists the melting points of the 3,5-dinitrobenzoates, phenyl urethans and α-naphthyl urethans for comparison.

From the above table it is evident that the *p*-nitrophenyl urethans possess a few advantages over the other derivatives. The general melting point range is higher, which makes them easier to recrystallize. In two instances the melting point difference does not permit absolute identification, namely, n-propyl and isopropyl alcohols and hexyl and heptyl alcohols.

Para-nitrophenyl urethans may be prepared by the reaction between an alcohol and either *p*-nitrophenyl isocyanate or *p*-nitrophenylcarbamyl

TABLE I

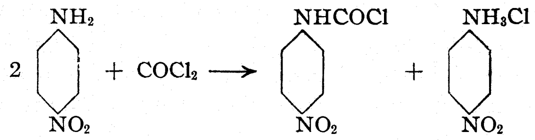
MELTING POINTS OF ALCOHOL DERIVATIVES

Alcohol	3,5-Dinitro-benzoate[1]	Phenyl urethan[2]	a-Naphthyl urethan[3]	*p*-Nitrophenyl urethan
Methyl	107.8	47	124	179.5
Ethyl	92 7	52	79	129
n-Propyl	73 0	58	105	115
Isopropyl	122.1	90	78	116
n-Butyl	62.5	Oil	71	95.5
Sec.-butyl	75.6	..	97	75
Isobutyl	86.5	80	104	80
n-Amyl	46.4		68	86
Isoamyl	61	55	67	97 5
Hexyl	58	..	59	103
Heptyl	46.9	68	62	102
Octanol-2	32.2	114	63	Oil
Ethylene glycol	..	157	176	135 5

chloride. Swartz[4] prepared *p*-nitrophenyl isocyanate by heating *p*-nitrophenylcarbamyl chloride which was obtained by the action of phosphorus pentachloride on ethyl *p*-nitrophenylcarbamate. The latter was made by the rearrangement of N-bromo-p-nitrobenzamide with sodium ethylate.[5]

Vittenet[6] prepared these reagents by the action of phosgene on *p*-nitraniline. Since the latter method makes use of readily available and inexpensive starting materials, a study was made of this procedure. Also, *p*-nitrophenylcarbamyl chloride was easier to prepare than the isocyanate and hence its preparation and use were studied.

When phosgene was passed into fused p-nitraniline similarly to the procedure used for phenyl isocyanate,[7] considerable charring and tar formation took place. Vittenet[6] refluxed together a toluene solution of p-nitraniline and a benzene solution of phosgene and succeeded in preparing *p*-nitrophenyl isocyanate in small amounts. As soon as phosgene is run into a solution of *p*-nitraniline in toluene, a precipitate of *p*-nitraniline hydrochloride separates.



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[1] Malone and Reid, THIS JOURNAL, 51, 3426 (1929). Students have difficulty in obtaining these melting points. The values for these diiitrobenzoates usually obtained are one to two degrees lower.

[2] Clarke, "Organic Analysis," Arnold and Co., London, 1928.

[3] French, Bickel and Wirtel, THIS JOURNAL, 48, 747, 1736 (1926).

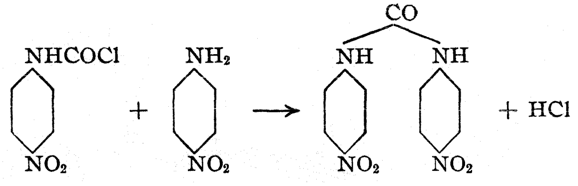
[4] Swartz, *Am. Chem.* J., 19, 318 (1897).

[5] Swartz, *ibid.*, 19, 301 (1897).

[6] Vittenet, Bull. *soc. chim.*, [3] 21, 587 (1899).

[7] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 10.

This reaction consumes half the p-nitraniline and also makes the reaction difficult to carry out because the undissolved p-nitraniline hydrochloride does not react with the phosgene. If a large amount of p-nitraniline is present in excess, a second reaction occurs as follows



The reaction mixture therefore contains all these substances and makes it difficult to obtain a pure reagent. Hence the best conditions call for a constant excess of phosgene to prevent the formation of substituted ureas, a temperature sufficiently high to prevent the precipitation of *p*-nitraniline hydrochloride and a good solvent for p-nitraniline. It was found that ethyl acetate was not only a good solvent for phosgene[S] but also a much better solvent for p-nitraniline than benzene or toluene, and therefore more suitable for the preparation of larger amounts of the reagent.

Although Swartz[4,5] reports that *p*-nitrophenylcarbamyl chloride decomposes at 56° to the isocyanate, the material obtained by the above procedure was always the acid chloride. Evidently the dissociation did not occur in ethyl acetate solution in the presence of phosgene and the hydrogen chloride produced in the reaction.

Experimental Part

Preparation of ***p*-Nitrophenylcarbamyl** Chloride.—The apparatus was set up as shown in Fig. 1. This arrangement permits the phosgene reaction to be carried out conveniently and without danger providing a good hood and exhaust fan are available.

Five hundred cubic centimeters of ethyl acetate was placed in the 5-liter round-bottomed Pyrex flask. Phosgene was bubbled slowly through the ethyl acetate until it was saturated. A solution of 150 g. of 9-nitraniline in 1500 cc. of ethyl acetate was run in slowly from the tap funnel over a period of from two and one-half to three hours. The addition of p-nitraniline must be at such a rate that the precipitate of p-nitraniline hydrochloride which is formed at first is allowed to dissolve and not accumulate. The mixture may be warmed if necessary. A steady stream of phosgene must be kept passing through the solution, and toward the end of the reaction the solution must be boiled gently to break up the p-nitraniline hydrochloride, as it dissolves quite slowly.

After the addition of the last of the p-nitraniline the stream of phosgene was continued for five minutes and then shut off. The flame under the flask was then turned up and the ethyl acetate distilled. The brown residue was treated with 800 cc. of hot carbon tetrachloride and the insoluble residue (the disubstituted urea) removed by filtration. About two-thirds of the carbon tetrachloride was distilled and the solution cooled. The *p*-nitrophenylcarbamyl chloride crystallizes and is filtered. By concentration of the mother liquor a further crop may be obtained. The product may be re-

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[8] Baskerville and Cohen, *Ind. Eng. Chem.*, **13**, 333 (1921).

crystallized again from carbon tetrachloride and yields light yellow needles, melting at 57°. The yield of crude product after one recrystallization was 210 g. (96.5% of the theoretical).

Anal. Subs., 0.2001: 20.0 cc. of 0.10 N HCl. Calcd. for $C_7H_5O_3N_2Cl$: N, 13.97. Found: N, 14.00.

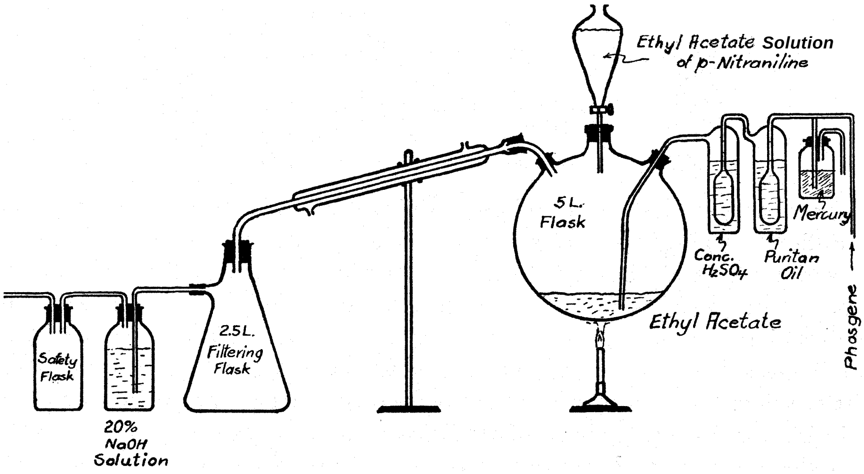

Fig. 1.

Preparation of **p-Nitrophenyl Urethans.**—It was found that the best method for making the urethans was to prepare a benzene solution of p-nitrophenylcarbamyl chloride and add a slight excess of the pure alcohol. The reaction usually takes place spontaneously with evolution of heat and is over in about five minutes. The benzene is distilled and an excess of cold carbon tetrachloride added together with a little norit. The solution is then filtered. This procedure removed any *sym.*-di-[*p*-nitrophenyl]-urea which may be formed by traces of water in the alcohol. Evaporation of the carbon tetrachloride to a small volume and cooling yields crystals of the urethan. The p-nitrophenyl urethans with their melting points and analyses are given in Table II.

TABLE II

PARA-NITROPHENYL URETHANS

Alcohol	M. p., °C.	Formula	Nitrogen analyses, % Calcd.	Found
Methyl	179.5	$C_8H_8O_4N_2$	14 28	14.10
Ethyl	129	$C_9H_{10}O_4N_2$	13.33	13.33
Propyl	115	$C_{10}H_{12}O_4N_2$	12.50	12.36
Isopropyl	116	$C_{10}H_{12}O_4N_2$	12.50	12.31
Butyl	95.5	$C_{11}H_{14}O_4N_2$	11.76	11.59
Sec.-butyl	75	$C_{11}H_{14}O_4N_2$	11.76	11.61
Isobutyl	80	$C_{11}H_{12}O_4N_2$	11.76	11.51
Amyl	86	$C_{12}H_{16}O_4N_2$	11.11	11.06
Isoamyl	97.5	$C_{12}H_{16}O_4N_2$	11.11	11.03
Hexyl	103	$C_{13}H_{18}O_4N_2$	10.53	10.09
Heptyl	102	$C_{14}H_{20}O_4N_2$	10.00	9.94
Ethylene glycol	135.5	$C_{16}H_{14}O_8N_4$	14.36	14.00

Summary

1. A procedure for the preparation of *p*-nitrophenylcarbamyl chloride has been worked out.
2. The *p*-nitrophenyl urethans of the common aliphatic alcohols are described.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 643]

THE SYNTHESIS OF SIMPLE AND OF SUBSTITUTED 2-ALKYLCINNAMIC ALCOHOLS, INCLUDING A MONOMOLECULAR CUBEBIN

BY MARSTON TAYLOR BOGERT AND GARFIELD POWELL[1]

RECEIVED FEBRUARY 11, 1931 PUBLISHED APRIL 6, 1931

Introductory

The appearance of the recent articles by Gomberg and Bachmann[2] and by Shankland and Gomberg,[3] lead us to publish some closely related work, carried out in 1929, reported at the Annual Convention of the American Manufacturers of Toilet Articles, New York, last April, and published last spring as part of the Dissertation submitted by the junior author for the Ph.D. degree at Columbia University.

The problem of reducing unsaturated aldehydes to the corresponding unsaturated alcohols has occupied the attention of organic chemists for many years and is a subject of considerable practical importance to the perfume industry.

Iron and acetic acid have been used on aldehydes[4] or on their diacetates,[5] but the methods are tedious and the yields unsatisfactory.

The reducing action of aliphatic Grignard reagents on aldehydes and ketones has been known for many years. Marshall's experiments: supported by the work of Meisenheimer[7] and of Shankland and Gomberg,[3]

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[1] Fritzsche Fellow for 1928–1929 at Columbia University. This investigation could not have been undertaken without the generous assistance of Mr. F. E. Watermeyer, President of Fritzsche Brothers, Inc., of New York, the donor of the Fellowship.—[M. T. B.]

[2] Gomberg and Bachmann, Tms JOURNAL, 52, 4967 (1930).

[3] Shankland and Gomberg, *ibid.*, 52, 4973 (1930).

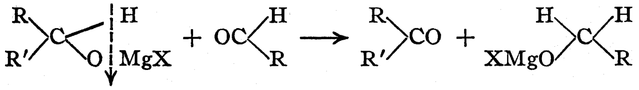
[4] (a) Herzig, Monatsh., 3, 123 (1882); (b) Lieben and Zeisel, *ibid.*, 4, 28 (1883); (c) *ibid.*, 7, 55 (1886).

[5] (a) Barbier and Leser, *Bull. soc. chim.*, [3] 33, 858 (1905); (b) Hill and Nason, THIS JOURNAL, 46, 2236 (1924); (c) Pauly, Schmidt and Böhme, Ber., 57B, 1329 (1924).

[6] (a) Marshall, *J. Chem. Soc.*, 105, 527 (1914); (b) 107, 509 (1915); (c) 127, 2184 (1925).

[7] Meisenheimer, Ann., 446, 76 (1926).

make it clear that is not the Grignard reagent itself which functions as the reducing agent in such cases, but the addition product formed by the reagent with the aldehyde, RCH(OMgX)R′, which is then oxidized by the excess of aldehyde, the latter being compensatingly reduced



Liittringhaus[8] patented a process of reducing aldehydes to alcohols by the action of ethyl alcohol in the presence of activated magnesium, the alcohol being oxidized simultaneously to aldehyde, and claimed the successful reduction of citronellal, geranial (citral) and cinnamic aldehydes to the corresponding alcohols.

Meerwein and Schmidt[9] discovered that $Al(OR)_3$, or ROMgX, in the presence of some free ROH, acting on aldehydes at moderate temperatures, gave 80 to 90% yields of the corresponding alcohols, the aldehyde and alcohol groups exchanging partners, the equilibrium being kept moving to the right by the removal of the aldehydic by-product as fast as it formed

$$RCHO + R'CH_2OH \rightleftharpoons RCH_2OH + R'CHO$$

Among the alcohols they secured in this way from their aldehydes, were geraniol and hydroxycitronellol.

Ponndorf,[10] by the use of a similar method, successfully prepared cinnamic alcohol, geraniol and nerol, carveol and other alcohols, from the corresponding aldehyde or ketone. As pointed out by Gibson and Simonsen,[11] dl-piperitol can thus be prepared readily from dl-piperitone.

Inasmuch as a compensating oxidation and reduction seems to be involved in the change, it has been likened[9] to the Cannizzaro Reaction.

The noteworthy fact remains, however, that when $Al(OR)_3$ acts upon mixtures of aldehydes and alcohols, the products are the same as when ROMgX is the catalyst, although aluminum does not form organic complexes of exactly the same type as magnesium.

Child and Adkins[12] carried out an interesting series of experiments, using aluminum ethoxide as catalyst to convert aldehydes into esters, $2RCHO \longrightarrow RCOOCH_2R$.

Adams and his co-workers[13] obtained an excellent yield of cinnamic alcohol by reducing cinnamic aldehyde with hydrogen in the presence of their platinum oxide–platinum black catalyst. Our experience with this method, however, has been that the conditions determining a satisfactory

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[8] Liittringhaus, German Patent 384,351 (1924).

[9] Meerwein and Schmidt, *Ann.*, 444, 221 (1925).

[10] Ponndorf, *Z. angew.* Chem., 39, 138 (1926).

[11] Gibson and Simonsen, Chem. *Industry*, 49, 540 (1930).

[12] Child and Adkins, THIS JOURNAL, 45, 3013 (1923).

[13] Adams and Tuley, *ibid.*, **47**, 3061 (1925); etc.

yield are highly specific, small variations in the proportions of the catalyst mixture, or changes in its activity, affecting the results profoundly, so that considerable experimentation would have been necessary to ascertain the optimum conditions in the case of each aldehyde.

For the reduction of certain cinnamic aldehydes we had on hand, the method of Meerwein and Schmidt proved entirely satisfactory and in this way 2-ethyl and 2-isoamyl cinnamic alcohol, 2-methyl-3-*p*-tolylallyl alcohol and 2-piperonylidene-ethanol, were prepared. The products were practically free from unchanged initial aldehydes, for simple fractional distillation under diminished pressure sufficed to give a pure alcohol, without any previous special chemical treatment for the removal of aldehydes.

The 2-piperonylidene-ethanol prepared by this method was not identical with the product obtained by Pauly, Schmidt and Böhme[5c] by reduction of the same aldehyde with iron and acetic acid, and to which they assigned the same formula. The reason for this discrepancy is under investigation and the results will be published later.

Natural cubebin was at one time assumed to be the 2-piperonylidene-ethanol, but recent researches, especially those of Mameli,[14] make it clear that its formula is much more complicated and, in support of this, the 2-piperonylidene-ethanol obtained by Pauly, Schmidt and Bohme, and the one prepared by us, are totally different from natural cubebin.

In general, these unsaturated alcohols decolorized a carbon tetrachloride solution of bromine much more rapidly than the corresponding unsaturated aldehydes, the color being discharged promptly until near the saturation point.[15]

Their boiling points were generally higher than those of the corresponding saturated or unsaturated aldehydes, saturated alcohols or propanes. Their odors were of the cinnamic alcohol type.

Experimental

2-Ethylcinnamyl Alcohol, $C_6H_5CH{=}C(C_2H_5)CH_2OH$.—A solution of 5.5 g. of dry hydrogen chloride in 100 cc. of absolute alcohol was prepared in a flask provided with a reflux condenser which carried a calcium chloride guard tube, and to this solution there was added 4 g. of clean magnesium ribbon. The reaction was completed by refluxing the mixture until all the metal was dissolved (one hour or longer). The air in the apparatus was then displaced by a current of dry nitrogen and, while this gas was kept passing through the refluxing mixture, 30 cc. of a-ethylcinnamic aldehyde was added through the condenser. The water in the condenser was not changed during this reaction and upon its completion had become sufficiently heated by the refluxing condensate so that the calcium chloride tube was removed and 40 cc. of alcohol was carried out in this way by the stream of nitrogen gas. After refluxing for about seven hours, the mixture was cooled, thrown into excess of water, the whole acidified with acetic acid, ether added, the

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[14] Mameli (a) *Gazz. chim. ital.*, 37, II, 483 (1907); (b) 39, I, 477 (1909); (c) 39, I, 494 (1909); (d) **42**, II, 546 (1912); (e) **42**, II, 551 (1912); (f) **51**, II, 353 (1921).

[15] Compare Reich, van Wijck and Waelle, *Helv. Chim. Acta*, 4, 242 (1921).

mass filtered from a small amount of resinous impurities, the ether layer separated, washed with sodium carbonate solution, to remove all acetic acid, then with water, dried and the solvent removed. The residue was fractioned under reduced pressure in an atmosphere of nitrogen and 22 cc. of a nearly colorless oil was collected at 127–137° (mostly at 137°) at 8 mm., leaving a viscous residue in the flask. When the fraction collected was redistilled (in nitrogen), practically all passed over at 131–132° (corr.) at 9 mm., as a colorless oil.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.42; H, 8.70. Found: C, 81.28; H, 8.86.

In this preparation, chloromagnesium ethylate was found to be far superior to aluminum ethylate. Meerwein and Schmidt[9] record a similar experience in the production of cinnamic alcohol from the aldehyde.

The viscous by-product remaining in our flask after taking off the fraction of b. p. 127–137° (8 mm.) yielded, with incipient decomposition, a fraction boiling at about 200° (4 mm.), containing 79.39% of carbon and 8.92% of hydrogen, but which was not investigated further.

The alcohol instantly decolorized carbon tetrachloride solutions of bromine, with no observable evolution of hydrogen bromide, whereas the corresponding unsaturated aldehydes take from seconds to minutes to discharge the color of such bromine solutions. The odor was weak but agreeable, similar in type to that of cinnamic alcohol itself. The alcohol was easily reduced to the corresponding 2-ethylhydrocinnamyl alcohol (2-ethyl-3-phenylpropyl alcohol) and 2-ethyl-3-phenylpropane (3-methyl-4-phenylbutane), by hydrogen in the presence of palladium (Skita method). It discharged the color of a dilute aqueous potassium permanganate solution when shaken with it.

p-Nitrobenzoate.—This was prepared from *p*-nitrobenzoyl chloride and the alcohol in the presence of pyridine; m. p. 110–111° (corr.).

Anal. Calcd. for $C_{18}H_{17}O_4N$: H, 5.5. Found: H, 5.68. Through an accident, the carbon determination was lost, and there remained insufficient material for purification and another combustion.

A **phenylurethan** also was produced by heating equal moles of the alcohol and phenyl isocyanate together in a sealed tube for six hours at 100°. By the addition of petroleum ether (b. p. 40–60") to the reaction product, crystals were obtained, m. p. 63–64° (corr.), whose melting point was unchanged by recrystallization from 75% alcohol.

2-*n*-Amylcinnamyl alcohol, $C_6H_5CH{=}C(C_5H_{11})CH_2OH$, was prepared similarly. The refluxing was continued for eleven and one-half hours, and the crude product separated as before and distilled in nitrogen, gave a main fraction, b. p. 144–165' (6 mm.). This was redistilled and the fraction, b. p. 141–143' (5 mm.) was a colorless oil of faint odor recalling that of cinnamic alcohol; yield, 50%.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.29; H, 9.88. Found: C, 82.15; H, 10.0.

The properties of this alcohol, so far as tested, were the same as those of the corresponding 2-ethyl derivative.

Phenylurethan.—A mixture of the alcohol with a slight excess of phenyl isocyanate was heated in a sealed tube for two and one-quarter hours at 100°. The excess of isocyanate was removed from the product by heating at 100° and reducing the pressure to 16 mm. Addition of petroleum ether to the residue precipitated a solid, which crystallized from dilute alcohol in colorless crystals, m. p. 61–62° (uncorr.).

2-Methyl-3-p-tolylallyl alcohol, $p\text{-}CH_3C_6H_4CH{=}C(CH_3)CH_2OH$, from 3.5 g. of magnesium, 5 g. of hydrogen chloride in 225 cc. of absolute alcohol, and 25 cc. of 2-methyl-3-p-tolylacrolein, refluxed for seven and one-half hours in an atmosphere of nitrogen, was worked up as in the case of the other alcohols and finally distilled. The portion coming over below 160" at 10 mm. on rectification gave a fraction, b. p. 142–143° (11 mm.), as a colorless oil, whose odor and other properties resembled those already described; yield, 60%.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.42; H, 8.70. Found: C, 81.39; H, 8.97.

2-Piperonylidene-ethanol (Monomolecular "Cubebin") was prepared from 4 g. of magnesium, 5 5 g. of dry hydrogen chloride in 225 cc. of absolute alcohol, and 23 g. of piperonylidene-acetaldehyde (m. p. 83–84"; b. p. 162–163" (5 mm.)). After refluxing for four hours (in nitrogen), the crude product was separated and distilled at 5 mm. pressure. Above 200°. considerable decomposition was evident. The distillate collected below this point yielded, on rectification, a fraction, b. p. 167–168° (5 mm.), which gave colorless crystals from benzene or alcohol, m. p. 78–78.8° (corr.).

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.39; H, 5.66. Found: C, 67.17; H, 5.95. Molecular weight (in camphor): Calcd., 178. Found: 173.

The yield before final purification was only about 20% (4 g.), but this was raised to approximately 30% when aluminum ethylate was used in place of the chloromagnesium ethylate.

Its reactions were similar to those of the other alcohols described in this paper. It decolorized instantly a carbon tetrachloride solution of bromine, or an aqueous permanganate solution. Reduced catalytically, the odor of dihydrosafrole was pronounced, one mole of hydrogen being absorbed in about ten minutes.

Benzoate.—The alcohol was condensed with benzoyl chloride in the presence of pyridine, and the purified product formed fine long colorless needles, m. p. 96–97' (corr.), which decolorized bromine solutions less rapidly than the alcohol itself.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.31; H, 5.0. Found: C, 72.21; H, 5.22.

Phenyl **Urethan.**—A mixture of the alcohol with an excess of phenyl isocyanate was heated in a sealed tube for four hours at 100°. As the tube cooled, the contents solidified. The crude product was dissolved in benzene, reprecipitated by the addition of petroleum ether and the precipitate then crystallized from a mixture of these two solvents. Small colorless needles were obtained, m. p. 96–97" (uncorr.).

Anal. Calcd. for $C_{17}H_{15}O_4N$: C, 68.66; H, 5.1. Found: C, 68.98; H, 5.11.

Summary

1. The 2-alkylated cinnamic aldehydes are very satisfactorily reduced to the corresponding cinnamic alcohols by the use of chlorornagnesium ethylate or aluminum ethylate.
2. The monomolecular "cubebin" prepared in this way differs from that recorded in the literature, which was obtained by reduction with iron and acetic acid.

NEW YORK, N. Y.

COMMUNICATIONS TO THE EDITOR

THE ABSORPTION OF WATER VAPOR BY COTTON CELLULOSE

sir:

In a paper by L. M. Pidgeon and O. Maass entitled "The Adsorption of Water by Wood" [THIS JOURNAL, 52, 1053 (1930)], figures are given for the adsorption of water vapor by purified cotton cellulose. The method of measurement was one that was selected by the authors after a consideration of the possible sources of error, since, they say, "Little of the work which has been done is entirely free from objection , . . . and . . . . in even the most careful determinations of the adsorption by cotton cellulose the amount of adsorption was measured indirectly."

The absorption of water vapor by cotton has formed the subject of systematic investigations extending over eight years by my colleagues, the late Dr. A. M. Williams and Dr. A. R. Urquhart. The methods used were submitted to critical examination, and the results of the investigation, which derive from observations on some hundreds of samples of cotton, are contained in the *Shirley Institute Memoirs*, and are being published in a series of communications to the "Journal of the Textile Institute," nine of which have so far appeared since 1924. A complete absorption and desorption isotherm for pure cotton cellulose at 25° is given in one of these communications [J. *Text. Inst., 15,* T433 (1924), or *Shirley Institute Memoirs,* 3, 197 (1924)], the latter of these two references being quoted by Pidgeon and Maass in their paper.

Since these authors have omitted to do so, and since the *Shirley Institute Memoirs* do not possess the wide circulation among scientific readers enjoyed by the *Journal of the American Chemical Society,* it seems desirable to call the attention of your readers to the fact that, at high relative humidities, there are gross discrepancies between the results of Pidgeon and Maass and those of Urquhart and Williams. Only one isotherm is given by Pidgeon and Maass, namely, at 23°, but this can be compared with the isotherm obtained by Urquhart and Williams at 25°, since it is clear from the work of both laboratories that this small difference of temperature can have no significant effect on the moisture absorption at a given relative humidity. The value obtained by Urquhart and Williams exceeds that given by Pidgeon and Maass by 11% at saturation, by 4% at 90% relative humidity, and by 2% at 80% relative humidity.

It is to be hoped that an attempt will be made to discover the source of the discrepancy, which must lie either in the technique of measurement or in the samples of "pure cotton cellulose." In this connection, it must be pointed out that the chemical attack of cotton cellulose by bleaching or otherwise, which increases its solubility in sodium hydroxide solutions, or reduces its so-called "a-cellulose" content, does not increase its moisture absorption at constant humidity, as Pidgeon and Maass would appear to expect on theoretical considerations, but has the opposite effect.

From the purely scientific aspect, the absolute values of the absorption may appear of less importance, as any errors of technique affecting all measurements would not necessarily invalidate conclusions drawn from the comparative behavior of different materials. Absolute values of the moisture absorption of cotton are, however, of the highest commercial and technical importance, since cotton is bought and sold on an agreed average moisture content, which can be defined from the absorption isotherm when the average conditions with respect to humidity and temperature are known. From this point of view alone it seems advisable to place on record the fact that the low figures of Pidgeon and Maass at high humidities—which will certainly surprise many technical workers experienced in the cotton processing industries—are much below those of other workers who have also devoted themselves to a long and critical examination of the subject.

THE BRITISH COTTON INDUSTRY
RESEARCH ASSOCIATION
SHIRLEY INSTITUTE, DIDSBURY
MANCHESTER, ENGLAND
ROBERT H. PICKARD

RECEIVED NOVEMBER 3, 1930
PUBLISHED APRIL 6, 1931

THE SUPERPOSITION OF ELECTRON CHARGES IN MOLECULES AND a-PARTICLES

Sir:

In their paper on the hydrogen molecule, Heitler and London[1] went to great length to stress the fact that the valence forces were not the ordinary coulomb forces, but were due to an exchange phenomenon involving the pair of electrons. Recent work by Slater,[2] Zener,[3] Bartlett[4] and others, raises the question as to whether Heitler and London have not overemphasized the importance of the exchange phenomenon. When we consider the exchange phenomenon we find that it has little objective significance; it may be described as a resonance effect in wave functions. On the other hand, the work of Slater and the others referred to above makes it clear that the bonding force between atoms is due to the overlapping or superposition of electron charge, the electron charge being treated as a distributed charge, whose density is proportion to $\psi\bar{\psi}$. In atoms with more than one valence electron, where the charge distribution is not spherically symmetrical, there is the possibility of a considerable

[1] Heitler and London, Z. *Physik*, 44, 455 (1927).

[2] Slater, Phys. Rev., 36, 57 (1930).

[3] Zener, *ibid.*, 36, 51 (1930).

[4] Bartlett, *ibid.*, 36, 1096 (1930).

bonding force, without the exchange phenomenon. When the exchange phenomenon is taken into account, a redistribution of charge is obtained with an increase in banding energy, but this increase is in some cases a small fraction of the total energy. It seems entirely probable that the "residual affinity" which has been invented to explain compounds such as B_2H_6 may be a result of overlapping of charge, without the exchange phenomenon.

It is perhaps not realized by chemists how revolutionary the idea of superposition of electron charges is, and how completely it removes the old difficulties with electrical charges and coulomb forces. The combination of two protons and two electrons in a stable arrangement is an impossibility; if the two electrons are superposed the repulsive forces between electrons disappear and a stable configuration is possible.

Of course, the complete superposition of charge does not occur ordinarily but one may wonder if it is not approached in the a-particle. The idea of the tetrahedral structure of the a-particle has suggested itself to many, and Latimer[6] has recently developed the idea in formulating a lattice structure for the nucleus. It is evident that a pair of electrons surrounded by four protons is subject to extraordinary forces and the superposition of the two electron charges might be nearly complete. The solution of this problem seems to lie within the present possibilities of wave mechanics, and the result would be of great interest.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

WORTH H. RODEBUSH

RECEIVED MARCH 18, 1931
PUBLISHED APRIL 6, 1931

ZIRCONIUM. III. THE REACTION BETWEEN AMMONIA AND METHYL ALCOHOLIC SOLUTIONS OF ZIRCONIUM SULFATE

Sir:

The fact that solutions of zirconium salts yield, upon the addition of ammonium hydroxide. a white gelatinous precipitate of zirconium hydroxide quite insoluble in water or in an excess of the precipitant has been known since the days of Berzelius. The results of recent work in this Laboratory tend to show, however, that under special conditions a compound other than the hydroxide may be precipitated by ammonium hydroxide if the zirconium sulfate be dissolved in methyl alcohol.

A methyl alcoholic solution of zirconium sulfate was treated with ammonium hydroxide or ammonia gas. Under ordinary conditions only the hydroxide would have been precipitated. If the solution be quite fresh, that is, if it has been prepared for only a matter of two or three minutes,

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[5] Latimer, THIS JOURNAL, 53, 981 (1931).

a white precipitate is obtained which is, strangely enough, quite soluble in water or in an excess of the precipitant. If the solution be allowed to stand for from five to ten minutes, only the hydroxide is precipitated. It was thought possible that the alcohol, employed as a solvent, either went into a direct-chemical reaction, or prevented hydrolysis from taking place as would have been the case if water had been employed as a solvent and to this end it was decided to carry out the experiments with a fresh water solution of zirconium sulfate in which hydrolysis had not taken place to any great extent. A solution of the age of three minutes yielded only the hydroxide upon precipitation with ammonia, and it was thought to be possibly too old. To this end the entire procedure of the preparation of the solution and precipitation by ammonia was reduced to ten seconds, then to five, but even in these cases only the hydroxide was obtained. It was considered that the amount of hydrolysis which could take place in five seconds would be very slight, and certainly would have had no great influence upon the reaction. Consequently it was considered that the presence of methyl alcohol was necessary for the reaction. Naturally this consideration does not account for the fact that old methyl alcoholic solutions yield only the hydroxide, and this will be discussed later.

A water solution of the precipitate was treated with the following reagents: ammonium hydroxide, ammonium carbonate, citric acid, and oxalic acid, all of which give characteristic precipitates with the zirconium ion. In no case was any reaction observed. When the solution was treated with barium chloride, however, a precipitate of barium sulfate was filtered off, and the filtrate resulting from this reaction readily gave precipitates with ammonium hydroxide and the other reagents mentioned above. When the usual analytical precautions were taken it was found that the precipitate lost **87.52%** by weight on ignition over a Fisher burner for forty-five minutes. Since the sample turned black during the course of ignition it was suspected that organic matter was present in the compound.

The fact that only fresh methyl alcoholic solutions of zirconium sulfate yield the soluble precipitate tends to indicate that some intermediate, and probably very complex, compound is formed between methyl alcohol and zirconium sulfate. Under ordinary conditions this compound probably decomposes very readily, but if the solution be used when fresh and treated with ammonium hydroxide, the ammonia enters the compound and forms a complex with zirconium in the anion. These conclusions, while not necessarily final, are supported by the evidence given above.

It is interesting to note that this phenomenon appears to take place with certain other elements such as aluminum and zinc, while such substances as magnesium and iron give no such reaction.

Work is now going on to the thorough study of these phenomena. Since the results are rather novel, however, this preliminary report has been prepared with the hope in mind that it might prove of some interest to those working with zirconium, especially since the complete research will not appear for some months.

3950 WALNUT STREET
KANSAS CITY, MISSOURI
HOWARD S. GABLE

RECEIVED FEBRUARY 11, 1931
PUBLISHED APRIL 6, 1931

THE ORTHO-PARA-HYDROGEN CONVERSION AT SURFACES

Sir:

Bonhoeffer and Harteck [*Z. physik.* Chem., **4B, 113** (1929)] found that nickel possessed a negligible activity for the reconversion of para-hydrogen to the ortho-para mixture even at room temperatures. Still less might one expect it to function as an agent for para-hydrogen formation at liquid-air temperatures. The data of Benton and White [THIS JOURNAL, 52,2325 (1930)] showed adsorption of hydrogen on nickel even at $-110°$ in an activated form [Taylor, THIS JOURNAL, 53,585 (1931)]. We have, therefore, carried out experiments on para-hydrogen formation with a very active nickel (10% nickel on kieselguhr) showing specific adsorptions for hydrogen of a much higher order of magnitude than the material employed by Benton and White. With this material we have shown it possible to produce the equilibrium concentration of 50% para-hydrogen at liquid-air temperatures as readily as on charcoal. That the surface activity was the important factor was readily shown by experiments with small fragments of nickel wire. With such, there was no measurable para-hydrogen formation.

We have extended these measurements to oxide surfaces since it has been found in adsorption studies [Garner and Kingman, Nature, **126**,352 (1930); Taylor and Williamson, THIS JOURNAL, **53**,813 (1931)] that below 0° there is no evidence of an activating adsorption of hydrogen but marked adsorption of molecular hydrogen. Our results on para-hydrogen conversion confirm this. Neither with an active zinc oxide nor with the more active hydrogenation agent zinc-chromium oxide is there any para-hydrogen formed at liquid-air temperatures even after fourteen hours' contact. On the contrary, in the temperature region where, on these surfaces, activated adsorption of hydrogen sets in, namely from 0° upwards, there is an immediate activity in the reconversion of the 50% para-hydrogen to the normal 1:3 mixture. The relative activities in this respect are exactly parallel with the influence of composition on the velocity of activated adsorption. Thus, with zinc-chromium oxide, the reconversion is complete in fifteen minutes' contact time at room temperature. With the less active zinc oxide it is barely perceptible in the same time at the same temperature and is not quite complete at 100° with the same time of contact. We are extending further this interesting method of determining the nature of hydrogen adsorbed on surfaces.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
HUGH S. TAYLOR
A. SHERMAN

RECEIVED MARCH 14, 1931
PUBLISHED APRIL 6, 1931

THE ALLOMERIZATION OF CHLOROPHYLL

Sir:

When an alcoholic solution of chlorophyll is allowed to stand, a process known as allomerization takes place.[1] Allomerized chlorophyll *a* differs from the original material in that the product of hot alkaline hydrolysis is a mixture of unstable chlorins instead of the normal product chlorin *e*. The same unstable chlorins are obtained from unallomerized chlorophyll or the magnesium-free compounds (phaeophytin *a* or methyl phaeophorbide *a*) by saponification with alcoholic alkali at room temperature or below. It has recently been established[2] that the essential change in both allomerization and low temperature saponification ("phase test" hydrolysis) is the dehydrogenation of the grouping —CHOHCO— to —COCO—. The fate of the two hydrogen atoms was, however, uncertain. We have now been able to show by very simple experiments that the hydrogen atoms are removed by the oxygen of the air. If allomerization or "phase test" saponification is carried out in a modified Warburg apparatus,[3] the absorption of oxygen is easily measured. The amount absorbed corresponds to the removal of two hydrogen atoms with the formation of hydrogen peroxide.

The dehydrogenation of chlorophyll *a* or the magnesium-free compounds in the *a* or b series may also be brought about by the use of potassium molybdicyanide in acetone–pyridine solution. Two equivalents of reagent are required per mole. Dehydrogenated chlorophyll *a* thus prepared is identical with allomerized chlorophyll (the ultraviolet absorption spectrum is a satisfactory method of distinguishing the dehydro compound from the original material). After removal of the magnesium from allomerized chlorophyll or chlorophyll dehydrogenated with molybdicyanide, the absorption spectrum in the visible and the ultraviolet is identical in both cases and indistinguishable from that of methyl dehydrophaeophorbide. This latter substance we have prepared in quantity by the action of molybdicyanide on methyl phaeophorbide *a*; it yields the unstable chlorins on hot alkaline hydrolysis.

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[1] Willstätter and Utzinger, Ann., 382, 129 (1911).

[2] Conant, Hyde, Moyer and Dietz, THIS JOURNAL, 53, 359 (1931).

[3] Hyde and Scherp, *ibid.*, 52, 3359 (1930).

From the facts given above, it is clear that allomerization is dehydrogenation brought about by the oxygen of the air. It is interesting that the dehydrogenation of a very easily oxidized group in chlorophyll is without pronounced effect on the color, although marked changes in color, as a rule, accompany the oxidation of a colored substance. The unusual behavior of chlorophyll in this respect is due to the fact that the chromophoric group is not the most easily oxidized group. A theory of photosynthesis has been recently suggested[4] which is based on the presence of this easily dehydrogenated group in chlorophyll.

CHEMICAL LABORATORY OF
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

J. B. CONANT
S. E. KAMERLING
C. C. STEELE

RECEIVED MARCH 23, 1931
PUBLISHED APRIL 6, 1931

NEW BOOKS

Fundamentals of Chemistry. By CARL WILLIAM GRAY, CLAUDE W. SANDIFUR and HOWARD J. HANNA. Revised and enlarged edition. Houghton Mifflin Company, 2 Park St., Boston, Massachusetts, 1929. xiv + 650 pp. 201 figs. 13 × 19.5 cm. Price $1.80.

This book is a revised and enlarged edition of a high school text, first published in 1924.[1] The order of presentation of the subject matter, used in the first edition, remains one of the original features of the book. This unusual order is characterized in part by the introduction of metals in Chapter III, metallic oxides and ores in Chapter VI, and the introduction of carbon as the third element considered. A new chapter on the structure of matter has been introduced before the chapter on ionization, obviating one criticism of the first edition. These two chapters now constitute a good elementary presentation of the electron concept, which, however, is not afterward utilized even in discussing such topics as the periodic classification and storage batteries, and only a limited use is made of this concept in the chapter on oxidation and reduction which has been added in this edition.

Other new chapters are entitled "The Atmosphere," "Paints, Varnishes and Lacquers," and "Chemistry in Agriculture." These titles indicate that the method of treatment and the subject matter are those conventionally associated with courses for school students not in the college preparatory group. However, it cannot be said that the fundamental generalizations have suffered. The illustrative material and the order of treatment constitute the chief differences from the conventional text.

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[4] Conant, Dietz and Kamerling, *Science*, 73, 268 (1931).

[1] Reviewed in THIS JOURNAL, 47, 592 (1925).

Preparatory school teachers, seeking this type of textbook, will find this volume well worth consideration. It is, in general, logically and clearly written, well illustrated and attractively arranged for student use, with outline summaries, questions and exercises at the close of each chapter.

C. R. HOOVER

Inorganic Chemistry for Colleges. A Textbook for Students of Second Year Chemistry. By WILLIAM FOSTER, Ph.D., Professor of Chemistry in Princeton University. Second Printing, 1930. D. Van Nostrand Company, Inc., 8 Warren Street, New York, 1929. viii + 837 pp. 212 figs. 14 × 22 cm. Price, $3.90.

A second printing a year after its publication indicates that this book has been well received. It is designed for students who have passed chemistry for entrance to college. The words, "A Textbook for Students of Second Year Chemistry," appear on the title page. While this book presupposes an elementary knowledge of the common elements, the descriptive side of chemistry has not been neglected; nor have the many applications of the science been slighted. The essential difference between this book and the average elementary college textbook lies in the more comprehensive treatment of fundamental laws and theories.

The book is divided into four parts, namely: Part I, (112 pages) is given to fundamentals, such as the laws of chemical combination, symbols, formulas, equations, the gas laws, the kinetic theory, the internal structure of crystals. Then an important and logical departure from the usual order of topics as found in other textbooks of this character: in Chapter IV, nearly 20 pages, the radioactive elements are studied in some detail in order to lay an experimental foundation for the study of atomic structure, which is considered in the following chapter on the classification of the elements.

Part II (386 pages), the non-metals, includes the usual descriptive matter, with separate chapters on solution; molecular and atomic weights; energy and chemical change; chemical equilibrium; the ionic theory and some of its applications; acids, bases and salts; oxidation and reduction from an electronic standpoint; colloid chemistry. While carbon is discussed in this part, organic compounds proper are left for Part IV.

Part III is devoted to the metals, the periodic classification being closely followed. A chapter on electrochemistry is placed between the tin and arsenic groups in the discussion of the metals.

Part IV (71 pages) called the supplementary part, is devoted entirely to organic compounds. The closing chapter is on The Food of Plants and of Animals. At the end of this section there is a good set of 144 problems with answers to most of them, which illustrate the principles taken up in the entire book.

At the end of each chapter a set of exercises is given and references for supplementary reading. The appendix contains the usual tables, also a four place table of logarithms, and the book closes with a bibliography of over one hundred titles.

HERMAN SCHLUNDT

General Chemistry. By HARRY N. HOLMES, Professor of Chemistry in Oberlin College, Revised edition. The Macmillan Company, 60 Fifth Ave., New York, 1930. x + 654 pp. 167 figs. 15 × 22.5 cm. Price, $3.50.

The revised edition of "General Chemistry" is a decided improvement over the first edition.

The author has succeeded in arranging the presentation of facts and theories in such a way that the student will never become "fed up" on one type of material. He has also included a good description of the various chemical processes that have become of great industrial importance and there is no better way of stimulating the interest of a Liberal Arts College student in chemistry than that of showing its relation to his own happiness and well-being.

His method of presenting the oxides of nitrogen before nitric acid is rather unusual. In fact his nitrogen question is rather confused but with this exception the book is very well written and should appeal to the teacher of General Chemistry.

It is not too hard for the student who has not had any previous training in chemistry and yet the introduction of considerable material in fine print makes it possible to arrange a course so that the student entering college with a good High School course in chemistry will find plenty to keep him busy.

This edition as well as the earlier edition will especially appeal to some teachers because the author has the courage to write equations at the beginning of the book. Teaching chemistry without equations is like trying to teach a language without a vocabulary. Equations should be introduced as soon as the first element is discussed.

The placing of Carbon and its oxides in Chapter IX and Sodium and Sodium Hydroxide Bases in Chapter XV is a help but leaving Equilibrium until Chapter XXIII is a decided weakness. Equilibrium conditions are encountered with the preparation of oxygen and it is regrettable that the author did not have the same courage with respect to equilibrium as he showed in writing equations.

The Periodic Table showing the Atomic Numbers in red is a particularly good feature.

It is a good text and the student will find it understandable as well as very interesting.

JOHN B. ZINN

Laboratory Manual of General Chemistry. By HARRY N. HOLMES, Professor of Chemistry in Oberlin College. Third edition. The Macmillan Company, 60 Fifth Ave., New York, 1930. x + 163 pp. 34 figs. 14.5 X 22.5 cm.

This laboratory manual is of the interleaved type. The subject matter is that usually found in a laboratory manual of first year college chemistry. The material is well arranged and the experiments are sufficient in number so that it is possible for the individual instructor to adapt the book to almost any type of laboratory course. Some of the experiments, marked with an asterisk, are rather difficult and well suited to those students who have had some previous training in chemistry.

In preliminary exercises, the time spent on the balance seems rather ill advised, but the chapter on Colloids would be a decided addition to any laboratory manual. The chapter on solutions is also very good and the set-up for the determination of the molecular weight of water on page 44 would keep the best student interested. The experiment using the Law of Du-Long and Petit is something different and a good addition.

The preparation of atomic models with toothpicks, chewing gum and soft wax seems rather childish. The chapter on equilibrium is very good but rather late in the course.

The book is especially well adapted to mixed classes made up of those who have had some training in chemistry and those who are studying chemistry for the first time.

On the whole it is a very good manual and is well worthy of the careful consideration of all teachers of General Chemistry.

JOHN B. ZINN

Chemistry in Daily Life. By SAMUEL GLASSTONE, D.Sc., Ph.D., F.I.C., Lecturer in Chemistry at the University of Sheffield. E. P. Dutton and Company, Inc., 286–302 Fourth Avenue, New York, 1929. vi + 250 pp. 21 figs. 13 × 19.5 cm. Price $2.25.

This book can be described as a textbook for the general reader. The author is content to chronicle in simple language the wonderful accomplishments of chemistry without attempting to present them as sensationally romantic. The content of the book can be judged by listing a few chapter headings: "The Beginnings of Chemistry"; "The Structure of Matter"; "Electricity and the Atom"; "Air and its Gases"; "Carbon and its Oxides"; "Our Daily Food; "Chemistry of Digestion"; "Catalysts and Enzymes"; and "Medicines and Perfumes." In short, the twenty chapters of the book cover the usual range of subjects included in popular chemistry, but they also include topics sometimes omitted.

The book is very sparsely illustrated, and, compared with some of our American school text and popular books on chemistry, would appear to be dry reading, but the clarity and simplicity of its style and the wide variety of general information presented compensate for this. In the opinion of the reviewer, it is a good reference book for the elementary student and of interest to the graduate who wishes to review his general knowledge of chemistry.

C. R. HOOVER

A Laboratory Manual of General Chemistry. By WILLIAM J. HALE, Director, Organic Chemical Research, Dow Chemical Company. Revised by William G. Smeaton, Professor of General and Physical Chemistry, University of Michigan. Revised edition. The Macmillan Company, 60 Fifth Avenue, New York, 1930. x + 530 pp. Illustrated. 13 × 20 cm. Price, $2.50.

"Eleven reprintings since this manual was first published in 1917 testify to its merit." It provides a series of experiments which can be coordinated with any standard textbook in general chemistry. The amount of experimental work given in the book is far more than can be covered in the first year course in general chemistry. The authors recognize this in the closing sentence of the preface: "By judicious selection from the experimental material offered, an instructor can organize a practical course of elementary general chemistry to meet any reasonable requirement."

After a chapter on general directions, Chapters II to XVII contain experiments on the common elements with one chapter on ionization and applications of the ionic theory. In this section of the manual a good balance is maintained between qualitative and quantitative experiments, but the latter are rarely required to be performed in duplicate. Chapter XVIII gives a systematic scheme for the identification of negative radicals. Chapters XIX to XXVI outline experiments on the metals. The final chapter contains notes on the procedure in qualitative analysis with a diagrammatic scheme for the identification of the common cations. The appendix contains seven very useful reference tables.

A notebook is not required as most of the pages are printed on but one side. This feature conserves the student's time for doing some thinking, which is demanded for intelligent performance of the experiments.

HERMAN SCHLUNDT

Principles of Chemistry. An Introductory Textbook of Inorganic, Organic and Physiological Chemistry for Nurses and Students of Home Economics and Applied Chemistry. With Laboratory Experiments. By JOSEPH H. ROE, Ph.D., Professor of Chemistry, George Washington University Medical School. Second edition. The C. V. Mosby Company, 3523–3525 Pine Boulevard, St. Louis, Mo., 1929. 427 pp. 13.5 × 20.5 cm. Price, $2.50.

This book is designed to meet the requirements of the short course in chemistry generally offered to nurses in training. There are 28 chapters of text, each followed by review questions,-in Part I, and 35 appropriately selected laboratory exercises in Part II. The book presents elementary chemical theory, very brief reference to elements other than oxygen, hydrogen nitrogen and carbon; few chemical formulas; and a simplified discussion of structural organic chemistry. Special emphasis is placed on the application of chemistry to life processes by the introduction of chapters on blood, internal secretions, digestion and metabolism.

Anyone who has attempted to teach the rudiments of chemistry to prospective nurses, undergoing the strenuous practical training of the average hospital course, realizes the need for making such a chemistry course as concise and practical as possible. The author has succeeded well in this endeavor.

It is not perhaps in accord with accepted educational methods of nurses' training to attempt to do more than the author has done to stimulate curiosity, originality and individual responsibility, but it seems that the average graduate nurse might well acquire more of these attributes in some part of her professional education.

C. R. HOOVER

Qualitative Analyse mit Hilfe von Tüpfelreaktionen. Theoretische Grundlagen und praktische Ausführung. (Spot Reactions in Qualitive Analysis. Theory and Their Practical Applications.) By DR. FRITZ FEIGL, Lecturer at the University of Vienna. Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany, 1931. xii + 387 pp. 12 figs. 2 colored plates. 16 × 24 cm. Price, unbound, M. 26.40; bound, M. 28.

Although the methods of qualitative inorganic analysis have not changed very much during the last century, the system is still far from being perfect. Therefore, any attempt to improve the situation must be welcomed by anyone interested in this field. Dr. Feigl has established his name in analytical chemistry by the discovery of a great number of qualitative and partly quantitative reactions for the detection and determination of various inorganic ions. A summary of his work (and that of others) and the fundamental principles on which it is based are given in this book, which is a valuable contribution to qualitative analysis and which discloses a field for systematic search of new organic reagents specific for metal ions and anions. This part of Feigl's work seems to be of more fundamental importance than the development of spot reactions on *a* spot plate or on filter paper, since the latter procedure does not introduce a new principle, although it must be admitted that this micro method has proved to be useful in cases where only small amounts of material are available. The theoretical part of the book dealing mostly on the properties of complex compounds (Werner) is well worth reading; this is especially true of Chapters 7 and 8 dealing with the specific action of organic compounds as a result of the presence of characteristic groups and on the influence of various organic groups on the solubility of complex compounds. In the practical part

(270 pages) various spot reactions for metal ions and anions are described and their applications to a systematic analysis and to purity tests are given. This part covers the literature fairly completely although the diethyl dithiocarbamate test for copper (Callan and Henderson, 1929), dinitroresorcinol for iron, copper and cobalt (Nichols and Cooper, 1923, 1925), thioglycolic acid for iron (Lyons, 1927), cysteine for cobalt (Michaelis and Yamagashi, 1928), aurintricarboxylic acid for aluminum, curcumin for beryllium and others might have been mentioned.

Without hesitation, Feigl's book can be recommended to anyone who is interested in the development of qualitative inorganic analysis. However, the reviewer wishes to point out that the book gives the impression that the results of the spot analysis may be favorably compared with those of micro-crystal reactions. But it should not be overlooked that the observation of the crystal form and a study of the crystal properties enables one to conclude with absolute certainty whether or not a certain constituent is present, whereas the simple color spot tests, useful as they may be, will never reach this degree of reliability and perfection.

I. M. KOLTHOFF

Elements of Chemical Engineering. BY WALTER L. BADGER, Professor of Chemical Engineering, and WARREN L. MCCABE, Assistant Professor of Chemical Engineering, University of Michigan. McGraw-Hill Book Co., Inc., 370 Seventh Ave., New York, 1931. xvii + 625 pp. Illustrated. 15.5 × 23.5 cm. Price, $5.00.

The recognition of chemical engineering as a distinct branch of engineering with its own peculiar body of facts and principles has been rapid since the widespread acceptance of the idea of the fundamental unit operations as its nucleus The well-known book by Walker, Lewis and McAdams was the pioneer in breaking away from the traditional type of text. The latter was essentially either a collection of facts and illustrations taken from trade catalogs or *a* description, accompanied by flow sheets and chemical reactions, of processes used in industry, many of which were obsolete. This book represented the first serious attempt to treat chemical engineering wholly from the standpoint of unit operations and to apply, in a comprehensive manner, fundamental principles of mathematics, physics, chemistry and economics to develop adequate quantitative theories of these basic operations.

The new text by Badger and McCabe covers nearly the same ground as the older book, but in a manner that is better suited to the needs of the beginner. All of the essential mathematical theory of the unit operations is included, but the approach to it is by an easier grade. The fundamental ideas upon which the mathematical development is based are more clearly explained and illustrated. It is the more elementary of the two texts, not in the sense that the more difficult theory has been omitted, but only that it has not been extended to so many different cases and more pains have been taken to present the underlying principles in a logical and orderly fashion so that they are more readily grasped by minds unaccustomed to thinking in abstract terms.

Practically all of the important unit operations of chemical engineering are covered, one chapter being devoted to each. An excellent balance is maintained between the theory of each operation and the practical art. The most important of the tools available to the chemical engineer in the practice of his art are well described with the aid of a large number of illustrations, which are clearly one of the outstanding features of the book. These are all line drawings, especially made for the book and have been admirably executed to show clearly the essential features of construction and to explain the principle of operation. The fact that there are somewhat more than half as many figures as there are pages in the book is convincing evidence of the extent to which visual aid to instruction has been utilized.

We venture to predict that this book will be widely adopted as the standard text for beginning students in chemical engineering and even for some more advanced courses. But one should not infer from this that its appeal is only to the student. On the contrary, its general excellence in both the theoretical and practical side of the subject is such that no one who has any contact with the technical side of chemical industry can afford to be without it.

BARNETT F. DODGE

Veröffentlichungen des wissenschaftlichen Zentral-laboratoriums der Photographischen Abteilung—AGFA. (Publications from the Scientific Laboratories of the Photographic Division—AGFA.) Vol. I. Issued by the I. G. Farbenindustrie Aktiengesellschaft. Verlag von S. Hirzel, Königstrasse 2, Leipzig C 1, Germany, 1930. vii + 155 pp. Illustrated. 94 figs. 17.5 × 24.5 cm. Price, RM. 10.

This first volume of a series to be issued by the I. G. Farbenindustrie Aktiengesellschaft contains a number of fairly elementary articles of interest to the spectroscopist, the photo-chemist, the color photographer, the Rontgenologist and the tone-film engineer, all treated from the standpoint of photographic technique. Articles by Eggert, Arens and others, on the theory of the latent image, the laws of blackening of the photographic emulsion and color sensitometry, are followed by a brief discussion of infra-red photography by Dieterle. Then come pages devoted to the use and control of photographic film in the talking movies. The next articles deal with x-ray problems, the first discussed being that of taking stereoscopic x-ray photographs, while the Agfa-Rontgen film dosimeter and its use constitute another.

The balance of the volume is taken up with a discussion of experiments on the thermal and other physical properties of cellulose and its derivatives, as of interest in photography; and with certain problems of half-tone reproduction. While as to unity of material the volume is a typical "Contributions from the ———Laboratory," it is well written and illustrated and nicely printed. A well selected bibliography accompanies each article.

GEORGE R. HARRISON

Chemical Calculations. By ERNEST L. DINSMORE, A.B., Chairman of the Chemistry Department, Boys High School, Brooklyn, New York. Globe Book Company, New York. vi + 182 pp. 7 figures. 12.5 × 19 cm.

The fourteen chapters of this book provide a "wealth of material in chemical calculations." In Chapters I to X inclusive the problems are arranged by types in the order in which the corresponding subject matter occurs in standard elementary texts on chemistry. Each chapter is introduced by some theoretical matter, definitions of chemical terms employed, and by the solution of one or more typical problems. A few study questions generally precede the numerical problems. Chapter XI comprises miscellaneous problems covering all the different types previously presented. Chapter XII includes 272 problems grouped under the chapter headings of the average textbook. These will be of special service in connection with review work, and will be helpful to teachers in the preparation of examination papers. Chapters XIII and XIV consist of 54 problems selected mainly from recent examination questions of the College Entrance Examination Board. No answers are given.

Some of the exercises in Chapter X, Solutions, deal with normal and molar concentration but problems based on Raoult's laws have been omitted. And there are no exercises on electrolysis—Faraday's laws—ionization constants, solubility product, P_H values, and calculations based upon oxidation–reduction reactions.

HERMAN SCHLUNDT

Reactions and Symbols of Carbon Compounds. A Textbook of Organic Chemistry. By T. CLINTON TAYLOR, Ph.D., Associate Professor of Chemistry, Columbia University. The Century Company, 353 Fourth Avenue, New York, 1930. x + 704 pp. 14.5 X 22 cm. Price, $4.00.

It should be stated at the outset that this is not "just another organic text." Professor Taylor has gone further than any other author your reviewer is aware of in presenting a course in theoretical organic chemistry on the basis of experiment. Despite the obvious difficulty of the undertaking, he has managed, in the main, to accomplish what he aimed to do. Students who really learn a considerable part of the material presented will know what reagents are actually employed to achieve certain ends, something, alas, which those brought up on the more conventional texts are liable to have altogether too little appreciation of.

The most glaring discrepancies in the book, and it must be admitted there are several, are evidently due to too hasty proof-reading. At least three proper names are misspelled, and other errors of spelling are easily discoverable. Too many formulas are incomplete, or actually wrong; for example, that for thymol indicates it to be an aldehyde, and nerolin is said to be an ethyl ether. Furthermore, the statement appears that "no acid chlorides (of oxalic acid) are known,') and this despite the fact that each set of the decennial indices to Chemical *Abstracts* presents numerous references to oxalyl chloride, which has been known for over fifteen years at least. The author, regrettably, consistently utilizes the term "symbol" where "formula" is the conventional designation, and offers no explanation for this eccentricity; also there are too many instances of the use of a term not yet explained, sometimes never explained, such as olefin, to cite a rather notable example. Sometimes where a preferable name, such as glycerol or pinacol, is mentioned by the author, he will subsequently content himself to use the older or less desirable nomenclature, which if we ever hope to arrive at a general usage of the preferable term is at least unfortunate. The modern interpretation of the Beckmann rearrangement is not given, and the formula for strychnine is, unhappily, not that on which Robinson's recent work has put the stamp of approval. The book is rather difficult reading at times because of the author's use of parenthetical expressions and references injected into the text; but, more particularly, footnotes are employed to an excessive extent, in one sentence characters appear referring the reader to three separate footnotes One extraordinary instance of lack of balance is evident; carbohydrates and rather closely related substances are given 82 pages out of 687 of actual text; whereas proteins are disposed of in **13.** One may be excused for riding an important hobby to the limit, but to back a favorite 6–1 is rather overdoing it.

It is always easy to find faults in anything and one should not infer from the foregoing that this text lacks attractive features. Those who have sought, too frequently in vain, for a good structural formula for mercurochrome, will be glad to find one included here. Electronic equations constitute a noteworthy feature of this text and **are** consistently and remarkably successfully employed.

When Professor Taylor's book appears in its next edition, more carefully proof-read, it will furnish a unique and thoroughly worth-while presentation of organic chemistry for college students.

G. ALBERT HILL

BOOKS RECEIVED

February 15, 1931–March 15, 1931

A. BEYTHIEN. "Laboratoriumsbuch für den Nahrungsmittelchemiker." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 589 pp. RM. 38, unbound; RM. 40, bound.

HERMAN T. BRISCOE. "Qualitative Chemical Analysis. Principles and Methods." D. Van Nostrand Company, Inc., 250 Fourth Ave., New York. 279 pp. $2.25.

CECIL W. DAVIES. "The Conductivity of Solutions and the Modern Association Theory." John Wiley and Sons, Inc., 440 Fourth Ave., New York. 204 pp. $4.00.

E. GILDEMEISTER AND FR. HOFFMANN. "Die Ätherischen Öle." Vol. III. Verlag der Schimmel and Co., Aktiengesellschaft, Miltitz bei Leipzig, Germany. 1072 pp. $9.50. "Register-Band." 124 pp. $1.50.

FRANZ KRCZIL. "Untersuchung und Beweitung technischer Adsorptionsstoffe." Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany. 504 pp. RM. 28, unbound; RM. 30, bound.

CARL S. MARVEL, Editor-in-Chief. "Organic Syntheses." An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. XI. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 106 pp. $1.75.

C. W. PORTER. "The Carbon Compounds." A Textbook of Organic Chemistry. Second revised edition. Ginn and Company. 15 Ashburton Place, Boston, Massachusetts. 469 pp. $4.00.

ERNEST RUTHERFORD, JAMES CHADWICK, AND C. D. ELLIS. "Radiations from Radioactive Substances." The Macmillan Company, 60 Fifth Ave., New York. 588 pp. $6.50.

JOHN C. SMOCK. "The Greek Element in English Words." Edited by Percy W. Long. The Macmillan Company. 60 Fifth Ave., New York. 356 pp. $15.00.

HANS WOLFF, W. SCHLICK AND HANS WAGNER, Editors. "Taschenbuch für die Farben- und Lackindustrie sowie für den einschlägigen Handel." Seventh edition. Wissenschaftliche Verlagsgesellschaft m. b. H., Tübinger Strasse 58, Stuttgart, Germany. 408 pp. RM. 12.50.

American Society for Testing Materials. "Proceedings of the Thirty-Third Annual Meeting." Held at Atlantic City, New Jersey, June 23–27, 1930. Volume 30, Part I, New and Revised Tentative Standards. Tentative Revision of Standards. Part II, Technical Papers. Published by American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa. Part I, 1336 pp. Part II, 1085 pp.